GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: October 18, 1976

Project Title: "Processing of Pitch-Based Staple Carbon Fiber into Yarn."

Project No: A-1912 (Sub-project - E-27-649/Textiles/Brookstein)

Project Director: Dr. D. J. O'Neil

Sponsor: Union Carbide Corporation, Parma, Ohio 44101

Agreement Period: From October 12, 1976 Until October 12, 1977

Type Agreement: Standard Industrial Research Agreement

Amount: $49,726 (Total authorized funding is $80,122; $30,396 budgeted in sub-project E-27-649)

Reports Required: Monthly Reports; Two Interim Reports.

Sponsor Contact Person (s):

Technical Matters

Contractual Matters
(thru OCA)

Union Carbide Corporation
12900 Snow Road
Parma, Ohio 44104

Defense Priority Rating: None

Assigned to: Productivity and Technology Applications (School/Laboratory)

COPIES TO:

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Project Code (GTRI)
Other

CA-3 (3/76)

no action
-2018
OH

GEORGIA INSTITUTE OF TECHNOLO
OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION

Date: February 27, 1978

Project Title: Processing of Pitch-Based Staple Carbon Fiber into Yarn

Project No: A-1912

Project Director: Dr. D. J. O'Neil

Sponsor: Union Carbide Corporation, Parma, OH 44101

Effective Termination Date: 12/12/77

Clearance of Accounting Charges: All clear.

Grant/Contract Closeout Actions Remaining: none

- _ Final Invoice and Closing Documents
- _ Final Fiscal Report
- _ Final Report of Inventions
- _ Govt. Property Inventory & Related Certificate
- _ Classified Material Certificate
- _ Other ____________________

NOTE: Sub-project is E-27-649/Brookstein/TE.

Assigned to: Technology & Development Laboratory (School/Laboratory)

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Project Code (GTRI)
Other ____________________

CA—4 (3/76)

ENGINEERING EXPERIMENT STATION
GEORGIA INSTITUTE OF TECHNOLOGY • ATLANTA, GEORGIA 30332

22 November 1976

Union Carbide Corporation
Carbon Products Division
Parma Technical Center
P.O. Box 6116
Cleveland, Ohio 44101

Attention: Mr. Robert C. Stroup and Dr. C.C. Troulson

Subject: Monthly Progress Report for EES Project A-1912, "Processing of Pitch-Based Staple Carbon Fiber into Yarn." Period: 10/12/76 to 10/31/76.

Gentlemen:

This report relates to the first two weeks of the subject project. (I attach a copy of the planned reporting schedule).

Part I. Technical Section

Virtually all of our effort in this period was devoted to forward planning for the next month, consolidation of individual efforts, and ordering of materials, supplies, and equipment vital for start-up.

The attached memorandum outlines the activities of this period.

Part II. Budget Section

Accounting statemnts for the month of October, 1976 indicate clearly that we are well within budget for this period. Expenditures and encumberances for the period are approximately $1600. A more representative picture of the budget situation should materialize with the November statemnt (next report).

Daniel J. O'Neil,
Program Manager

REPORT DUE DATE SCHEDULE

Date October 18, 1976

Project No. A-1912

Page 1 of 1 Pages

Project Title "Processing of Pitch-Based Staple Carbon Fiber into Yarn."

Contract/Grant No. Standard Ind. Res. Agreement

Project Director(s) Dr. D. J. O'Neil

Unit PTAL Initiation/Termination Dates 10/12/76 - 10/12/77

Prepare reports in accordance with:

1. Page 2 & 3 of Agreement.
2.
3.

NOTE: Deliver completed reports to ORA Reports Coordinator & the Photo Lab for recording, mailing and internal distributi If mailing & internal distribution is accomplished by Projec Director, please furnish two copies to ORA for record purpos

			APPROVAL DRAFT				APPROVED COPY				DATE MAILED
			At ORA		At Sponsor		At ORA		At Sponsor		
Designated Report Type	Rept. No.	Period Covered	Due Date	Min. No. Req.	Due Date	Min. No. Req.	Due Date	Min. No. Req.	Due Date	Min. No. Req.	
Monthly Report	1	10/12/76 - 10/31/76					11/8/76	7	11/10/76	2	
Monthly Report	2	11/1/76 - 11/30/76					12/8/76	7	12/10/76	2	
Monthly Report	3	12/1/76 - 12/31/76					1/8/77	7	1/10/77	2	
Monthly Report	4	1/1/77 - 1/31/77					2/8/77	7	2/10/77	2	
Interim Report		10/12/76 - 2/28/77					3/13/77	7	3/15/77	2	
Monthly Report	5	3/1/77 - 3/31/77					4/8/77	7	4/10/77	2	
Monthly Report	6	4/1/77 - 4/30/77					5/8/77	7	5/10/77	2	
Monthly Report	7	5/1/77 - 5/31/77					6/8/77	7	6/10/77	2	
Monthly Report	8	6/1/77 - 6/30/77					7/8/77	7	7/10/77	2	
Interim Report		3/1/77 - 7/31/77					8/13/77	7	8/15/77	2	
Monthly Report	9	8/1/77 - 8/31/77					9/8/77	7	9/10/77	2	
Monthly Report	10	9/1/77 - 9/30/77					10/8/77	7	10/10/77	2	
Final Report											

DISTRIBUTION: Project Director; School Director; ORA Reports Office; File

RA-76 (11-72)

18 October 1976

Minutes of Meeting

Meeting: Project A-1912, M-1
Date: 15 October 1976
Time: 1400-1600 hours
Attendance: D. O'Neil, D. Brookstein, A. Colcord

	ACTION
(1.) Task 1.0 Union Carbide Process. Brookstein to meet Union Carbide personnel (Stroup et al) in Greenville, S.C. for familiarization and selection of samples. Nov. 3-4, 1976	Brookstein
(2.) Task 2.0 Characterization. Properties such as coefficient of friction, individual tensile strengths, etc. would be measured at EES-ASL and, if possible, U.C. fiber length distribution might be more effectively measured by a "Quantimet"-type process in EES-ASL rather than by a T.E. technician	O'Neil & Brookstein
(3.) Process Schematic. D. Brookstein outlined a proposed process for attenuation/orientation/condensation/consolidation (Frame A) which includes modifications of concepts presented in the contract proposal. D. O'Neil presented a brief summary of possible bonding systems and processes (Frame B). A. Colcord commented on a cigarette-wrapper process that might be applicable to the process. It was agreed that maximization of process data would be a secondary goal of all experiments, e.g. mass losses of incoming fibers would be measured. It was agreed that a schematic illustration of the proposed process would be drawn and presented at the next meeting.	Brookstein and O'Neil
(4.) Physical Plant. The project will be conducted in an isolated room in the School of Textile Engineering. An intercom system has been installed. The room will be kept locked. Equipment purchased under this project will be used solely for this project. Materials	

(continued) 18 October 1976

	ACTION
and equipment purchases will be made through EES (Barbara Allen). O'Neil has arranged for D. Brookstein to make authorized purchases. A. Colcord will have major responsibility for the day-to-day maintenance of equipment and technician direction (A. Colcord has highest "time" involvement). All equipment and materials purchases will be reported to D. O'Neil.	All

(5.) Short-Term Schedule

Week Beginning	Task	
18 October 1976	Summarize weekly meeting	O'Neil
	Purchase: Workbenches and shop vacuum	O'Neil
	Specify equipment list for D. O'Neil	D. Brookstein
	Prepare schematic of process (Frame A)	D. Brookstein
25 October 1976	Equipment purchases. Preliminary set-up. Prepare lab.	Brookstein & Colcord
	Machining of parts	D. Brookstein
	Finalize schematic process (Frame B)	O'Neil
1 Nov. 1976	Decide properties of mat. required	All
	Greenville visit (3 & 4 Nov.)	D. Brookstein
	Post Greenville de-briefing and assignments	All
8 Nov. 1976	Characterization of mat. & fiber samples	Brookstein & O'Neil
	Process set-up	Brookstein & O'Neil
	Review of process-requirements vis-a-vis samples	All

(continued) 18 October 1976

	ACTION
N.B. Mr. Colcord's involvement will rise from approximately 20% to 50-60% during this period.	
(6.) Weekly Meetings	
Until further notice all meetings will be held on Friday afternoons at 3 p.m. in either the EES or at T.E. Next meeting: EES conference room, 22 October 1976.	All

Report A-1912-2

ENGINEERING EXPERIMENT STATION Georgia Institute of Technology

15 December 1976

Union Carbide Corporation
Carbon Products Division
Parma Technical Center
P.O. Box 6116
Cleveland Ohio 44101

Attn Mr. Robert C. Stroup and Dr. O.C. Troulson

Subject Monthly Progress Report for EES Project A-1912 "Processing of Pitch-Based Staple Carbon Fiber into Yarn." Period 11/1/76 - 11/30/76.

Gentlemen

This report summarizes our activities for the month of November describes plans for the month of December. and accounts for budgetary expenditures for November and October (total project time to 11/30/76).

PART I. TECHNICAL SECTION

1.0. "Task I. Familiarization with Process and Sample Selection"

Dr. Brookstein met with UC personnel in Greenville N.C. A 4 x 4 sampling scheme was designed. Two parameters (1) "fiber diameter" and (2) "process time during oxidation step" (related to tensile strength) were used to characterize the process and product. Samples were obtained by varying process conditions. Four levels for each parameter were selected (4 x 4) and another sample a "control" was obtained which has an intermediatediameter and an intermediate process (oxidation) time. (Correction the "control" has the longest oxidation time and presumably the highest tensile strength).

The actual process conditions for each of the seventeen samples are recorded by Union Carbide personnel. The information was not recorded by Dr. Brookstein. Code numbers are used so that UC personnel may related our findings to their process conditions.

2.0. "Task 2. Characterization of Sample Mats."

2.1. Fiber Length and Aspect Ratio. - One hundred was determined to be a statistically-representative number for characterization of fiber length within a mat. Testing is under way and will be completed in December.

page 2

Preliminary results show that the mats have a very wide distribution of lengths of fibers with coefficients of variation in the region 40-45%.

Summary of Partial Study on Fiber Length

SAMPLE CODE	#323	#322	#423	#6 ("Control")
FIBER LENGTH (mean value)	4.7 cm	4.1	3.1	4.5
STANDARD DEVIATION	1.9 cm	1.8	1.4	2.0
COEFFICIENT OF VARIATION	40.2 %	44.0	45.1	45.0
FIBER DIAMETER	7.7 Micron	7.7	7	11.7
ASPECT RATIO	6091	5324	4357	3850
Coefficient of Varaiation Ratio (Length/Diameter)	0.69	0.76	0.99	1.15

Fiber diameter values originate from Union Carbide. It should be noted that we have observed considerable variation in fiber diameter along individual fibers!

2.2. Tensile Properties. - Tensile properties using single fiber test procedures with an Instron are being undertaken. If difficulties are encountered the samples might be tested on the microtensile test apparatus of the EES Micromechanics Lab.

Peeliminary measurements indicate that problems in the reliability of tensile property data exist. It has been observed that indavidual isolated fibers are naturally bent. Hence they might be expected to fail in bending rather than in tension. However, it appears to us on the basis of our limited observations that the fibers fail at the "thick(er" spots along its length and in tension not in bending! A close examination of this apparent failure mechanism will be undertaken as part of the testing program.

2.3. Coefficient of Friction - Arrangements for determination of the coefficient of friction on individual fibers are being made with the Micromechanics Lab.

3.0. Process Development

All equipment has been ordered and received for the construction of Frame A. sub-system for attenuation and orientation. The machine shop has constructed the actual frame for precise mounting of components e.g. rollers motors etc. It was decided that sintered metal rollers would be used. Rapid delivery was accomplished and these rollers are now undergoing treatment to enhance their prosity. The vacuum system and expansion chamber have been received.

December's activities will center on the installation of the process equipment and preliminary commissioning, as well as design of the "consolidation" sub-system (Frame A'). Samples of industrial adhesives for binder systems are being requested.

PART II. BUDGET SECTION

Belated issuance of the accounting report for the month of November caused the slight delay in issuance of this report.

Unfortunately, the expenditures of Textile School personnel have not been received. It appears that an adjustment in our reporting schedule will facilitate the reporting of exact expenditures.

Summary of Expenditures to 11/30/76 (minus Textile)

PERSONAL SERVICES (Salaries)	$1817.02	1817.02
RETIREMENT	28.76	28.76
MATERIALS AND SUPPLIES	626.31	
	178.27	
	804.58	804.58
Travel	150.00	150.00

Rate of current expenditure = c. 10% of Budget

Time expended/Budgeted time = 13%

The estimates which includes that for Textile School personnel indicates that the program is being manged well within fiscal constraints.

Daniel J. O'Neil

Program Manager

A-1912

ENGINEERING EXPERIMENT STATION
GEORGIA INSTITUTE OF TECHNOLOGY • ATLANTA, GEORGIA 30332

23 February 1977

Union Carbide Corporation
Carbon Products Division
Parma Technical Center
P.O. Box 6116
Cleveland, Ohio 44101

Attn: Mr. Robert C. Stroup and Dr. O.C. Troulson

Subject: Combined Monthly Progress Report(s) for EES Project A-1912, "Processing of Pitch-Based Staple Carbon Fiber Into Yarn." Period: 12/1/76 - 1/31/77 (Reprts. A-1912-3/4)

Gentlemen:

This report summarizes our activities on your behalf for the month of December, 1976 and for January, 1977. As indicated in our last (monthly) report of 12/15/76 (Part II, Budget Section), we anticipated a delay in our reporting schedule in order to facilitate more accurate reporting of budget control. This factor, and the rapid development in this R&D effort, coupled with the fact that Dr. Brookstein has made a verbal report in Parma in January, has led to the presentation of our results in a combined report. A detailed interim report is in preparation at the moment and will analyze the overall results of this project for the period, 10/12/76 - 2/28/77, as agreed at the outset of this contract.

PART I. BUDGET SECTION

	% Time Expended	%* Budget Encumbered & Expended*
To 12/31/76	20 (2.5 mos)	17
To 1/31/77	30 (3.5 mos)	26 (est)

* Total Operating: $76,372

PART II. TECHNICAL SECTION

1.0. PROCESS DEVELOPMENT

ORIENTATION ACHIEVED! One of the most difficult fundamental tasks in this feasibility study has been undertaken with success. The randomly oriented mat has been processed to align individual fibers in a predominantly unidirectional orientation.

A rough schematic diagram of the process is presented in Figure 1. This is very definitely not drawn to scale. Photographs of the hardware have been given to you on Dr. Brookstein's recent visit to Parma. Brookstein and Alton Colcord will apply for a patent on the process, which relies on the use of perforated metal rollers.

Refinement of the process is underway in order to achieve consolidation of the oriented assembly ("yarn") into a cohesive, bonded yarn.

Consolidation may be effected exclusively by adhesive bonding as originally envisaged or by a process which might begin with a leading thread around which the oriented fibers might be wrapped. Subsequent bonding might follow with an adhesive system. The effect of incorporation of a continuous, single filamentary thread has not been assessed as yet.

Details of the orientation operation and the hardware will be presented in the forthcoming interim report.

2.0. BONDING

Numerous adhesives, coatings, and paint producers have been contacted and consulted for samples of candidate binders for the consolidation of the aligned fiber assembly (crude "yarn") into a Twistless Bonded Yarn or its analog.

Typical polymeric systems which have been received are listed below:

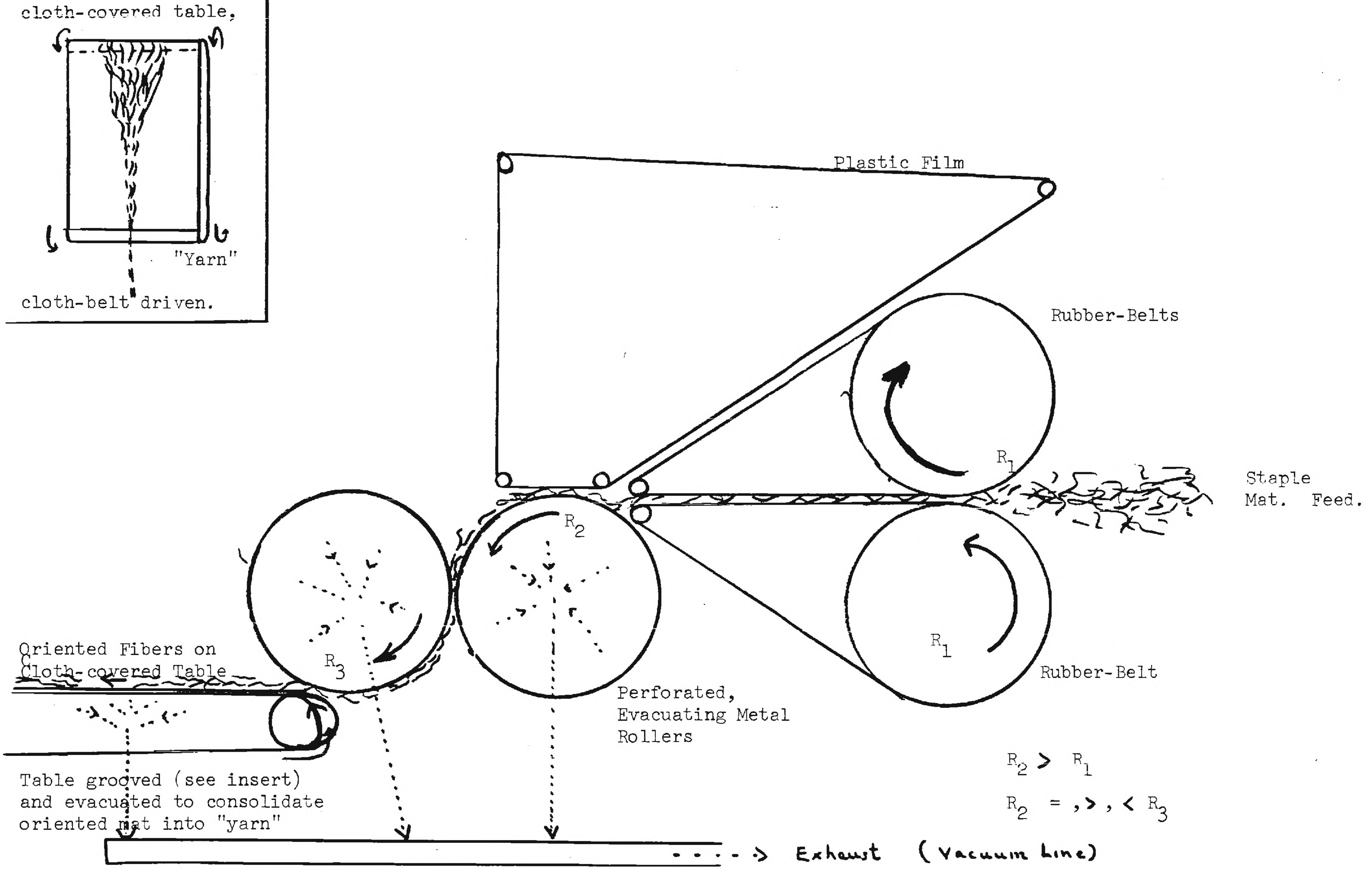


FIGURE 1. FRAME A - ATTENUATION/ORIENTATION OPERATION

(a) polyvinyl acetate homopolymer latex

(b) vinyl acetate-acrylic copolymer emulsion

(c) styrene-butadiene copolymer latex

(d) pre-plasticized vinyl chloride copolymer latex

(e) vinyl-acrylic terpolymer latex

(f) powdered polypropylene resin

(g) polyethylene emulsion

Suppliers include Union Carbide (Chemicals and Plastics Div.), Borden Chemicals, National Adhesives, Hercules, and others.

Dr. Bernard Eckstein of the Carbon Products Division has provided a sample of ethylene-acrylic acid copolymer latex which has been found to be effective for weaving of Thornel 300 materials.

Evaluation of films is undertaken firstly.

3.0. CHARACTERIZATION OF SAMPLE MATS AND FIBERS

(a) The dimensional properties of the sample carbon fiber mats which were obtained in Greenville have been characterized completely. Results are summarized in Table I. Full data will appear in the interim report.

(b) The tensile properties of the carbon fiber mat samples had been nearly completed during the subject period. (Complete results through mid-February are given). Table II (unlabeled) summarizes the results of these analyses which were obtained on an Instron.

(c) Fiber-fiber friction properties have not as yet been completed because of the special mounting techniques which are required to prevent breakage. Results are expected for inclusion in the interim report.

Table I
Dimensional Properties of Carbon Fibers

No.	Type	Diameter, μ			Length, cm			Aspect Ratio
		Mean, μ	SD, u	VC, %	Mean, cm	SD, cm	VC, %	
1	132	10.5	4.0	38.5	3.79	1.71	45.2	3609
2	133				3.14	1.66	52.7	2990
3	131				4.38	1.93	44.1	4171
4	120				2.54	1.18	46.6	2419
5	322	7.7	4.4	57.9	4.10	1.80	44.0	5324
6	323				4.69	1.89	40.2	6091
7	330				2.72	1.25	46.4	3532
8	321				4.69	2.04	43.6	6091
9	423	7.0	3.2	45.52	3.05	1.38	45.1	4357
10	422				3.95	1.78	45.1	5643
11	430				2.46	0.94	38.4	3514
12	421				3.66	1.79	49.0	5229
13	522	14.4	5.4	37.8	4.09	1.99	48.6	2840
14	530				2.71	1.17	43.1	1882
15	521				4.34	1.82	42.0	3014
16	6	11.7	4.6	39.1	4.54	2.04	45.0	3880

No.	Sample	Diameter, μm	Density, g/cm³	Linear density, den (tex)	Breaking load, pounds (gf): Mean value, pounds (gf)	Standard deviation, pounds (gf)	Variation coefficient, %	Specific strength, psi (Tenacity gf/den): Mean value psi (gf/den)	Standard deviation psi (gf/den)	Variation coefficient, %	Breaking extension, %: Mean value, %	Standard deviation, %	Variation coefficient	Young modulus, psi (Tensile modulus, g/den)
1	132	10 5	1.35	1.05 (0.11)	6.2×10^{-3} (2.82)	2.8×10^{-3} (1.26)	44.8	46321 (2.68)	20752 (1.20)	44.8	7.56	2.78	36.9	0.6×10^{6} ([illegible])
2	133				6.3×10^{-3} (2.86)	2.3×10^{-3} (1.04)	36.4	46978 (2.71)	17100 (0.99)	36.4	2.83	0.79	28.6	1.7×10^{6} (95.[illegible])
3	131				5.6×10^{-3} (2.56)	2.2×10^{-3} (1.0)	38.9	42050 (2.43)	16357 (0.95)	38.9	4.67	2.47	52.9	0.9×10^{6} (51.[illegible])
4	120				Breaking Load showed to be less than 0.5g									
5	322	7.7	1.35	0.57 (0.06)	7.3×10^{-3} (3.31)	1.7×10^{-3} (0.79)	23.9	101100 (5.85)	24163 (1.39)	23.9	2.94	0.79	26.9	3.4×10^{6} (198.[illegible])
6	323				6.0×10^{-3} (2.71)	2.1×10^{-3} (0.97)	35.9	82774 (4.78)	29715 (1.72)	35.9	3.0	0.68	23.0	2.8×10^{6} ([illegible])
7	330				Breaking Load showed to be less than 0.5g									
8	321				6.2×10^{-3} (2.82)	2.0×10^{-3} (0.93)	33.0	86133 (4.97)	28424 (1.64)	33.0	2.78	0.68	24.1	3.1×10^{6} ([illegible])
9	423	7.0	1.35	0.47 (0.05)	3×10^{-3} (1.35)	2.0×10^{-3} (0.89)	65.7	49893 (2.89)	32780	65.7	2.15	0.89	41.5	2.3×10^{6} ([illegible])
10	422				5.2×10^{-3} (2.36)	2.6×10^{-3} (1.16)	49.2	87036 (5.03)	42822 (2.47)	49.2	2.98	0.94	31.0	2.9×10^{6} ([illegible])
11	430				Breaking Load showed to be less than 0.5g									
12	421				5.0×10^{-3} (2.27)	1.7×10^{-3} (0.79)	35.0	83821 (4.84)	29337 (1.69)	35.0	3.39	0.84	24.3	2.5×10^{6} (143.1)
13	522	14.4	1.35	1.98 (0.2)	7.0×10^{-3} (3.18)	3.4×10^{-3} (1.53)	47.9	27772 (1.60)	13303 (0.83)	47.9	2.83	0.68	24.8	1.0×10^{6} ([illegible])
14	530				Breaking Load showed to be less than 0.5g									
15	521				6.5×10^{-3} (2.97)	2.6×10^{-3} (1.18)	39.6	25938 (1.49)	10271 (0.59)	39.6	2.99	0.63	21.7	0.9×10^{6} (50.2)
16	6	11.7	1.35	1.31 (0.14)	6.3×10^{-3} (2.87)	2.7×10^{-3} (1.21)	42.31	37968 (2.19)	16060 (0.93)	42.3	3.2	1.21	37.92	1.2×10^{6} ([illegible])

PART III. SUMMARY

Work is proceeding on schedule. In fact with the breakthrough by our engineers, the probability of success in this feasibility study is significantly increased.

Expenditures and encumbrances are well within the projected budget.

PART IV. FUTURE WORK

(a) Preparation of detailed interim report.

(b) Completion of characterization.

(c) Selection of Candidate Mats

(d) Refinement of Frame A orientation process

(e) Development of yarn bonding process

Respectfully submitted,

Daniel J. O'Neil,
Program Manager

Copies: Office of Contract Administration (2)
Dr. David Brookstein
Mr. Alton Colcord
Mr. R.L. Yobs

ENGINEERING EXPERIMENT STATION
GEORGIA INSTITUTE OF TECHNOLOGY • ATLANTA, GEORGIA 30332

July 5, 1977

Union Carbide Corporation
Carbon Products Division
Parma Technical Center
P. O. Box 6116
Cleveland, Ohio 44101

ATTENTION: Mr. Robert C. Stroup and Dr. O. C. Troulson

SUBJECT: Combined Monthly Letter Report(s) for EES Project A-1912, "Processing of Pitch-Based Staple Carbon Fiber into Yarn." Period: April 1, 1977 to May 31, 1977 (Reports A-1912--6/7)

Gentlemen:

This report briefly summarizes the financial and technical status of our project for the period April 1, 1977 until May 31, 1977. The first interim report reviewed our work and summarized budgetary expenditures through May 31, 1977.

Part I summarizes our operational budget through May 31, 1977.

Part II summarizes current and planned activities.

Respectfully submitted,

Daniel J. O'Neil
Project Manager

PART I. BUDGET SUMMARY

Period: 10/12/76 -- 5/31/77

Time Exhausted: 7.6 months

Time Remaining: 4.4 months (36.7%)

TOTAL

CONTRACT	$ 80,122
Patent Rights	3,750
Operational Budget	$ 76,372

	BUDGET	EXPENDED/ ENCUMBERED	BALANCE	% REMAINING
Personal Services	39,679.00	22,589.95	17,089.05	43.0
Retirement	3,611.00	1,421,98	2,189.02	60.6
Materials and Supplies	5,000.00	3,705.15	1,294.85	25.9
Travel	1,100.00	360.29	739.71	67.2
Total Direct Charges	49,390.00	28,077.37	21,312.65	43.2
Overhead	26,982.00	15,055.17	11,926.83	44.2
TOTAL	76,372.00	43,132.54	33,219.46	43.5

PART II. CURRENT AND PLANNED TECHNICAL ACTIVITIES

The work during this period focused on improving the uniformity of the web being produced by our vacuum-assisted opening process. Continued modification of the process and optimization of operating conditions was undertaken. In order to improve uniformity of the web by doubling (averaging thick and thin areas), the design and fabrication of an additional drafting system to the machine configuration, defined in Figure 3 of the First Interim Report, was being done. The initial unit had to be further modified due to belt slippage.

During this period, Dr. Brookstein visited Greenville to select a second set of mat samples for which specific process conditions were identified. These samples proved to be very difficult to process on our opening system, particularly when compared to the results with the first set of mat samples. A decision was made during the visit of Drs. Troulson and Schultz to Georgia Tech to transport our opening system to Greenville in order to screen and select processible mat samples.

An investigation of an alternate spinning method, open-cup spinning, was planned for the "pre-ox" carbon mat at the USDA laboratory in New Orleans. The USDA has a patented process for a relatively mild process of open-cup spinning, based on use of cotton. It is planned to admix "pre-ox" carbon and cotton fibers to test the feasibility of producing a hybrid fiber, which can act as a carbon yarn precursor.

Characterization of mat alignment and integrity was continued using scanning electron microscopy.

An increasing emphasis was placed on exploring the possibility of direct use of the aligned web, prior to yarn spinning. A program for composite fabrication and testing was initiated using a procedure which was suggested and demonstrated by Dr. Einstein of Union Carbide at our laboratories. This composite program was begun at the end of this report period and is aimed at a preliminary evaluation of, (1) the alignment of our mat and, (2) at the potential increase in mechanical properties which might be realized with the aligned mat composites.

TABLE OF CONTENTS

SUMMARY

Over the six month period (October 1976 to March 1977) significant progress has been made towards the goal of manufacturing staple yarns from pitch-based carbon fiber. A system for attenuating and aligning fibrous mat has been developed. This system is unique in that alignment and attenuation are affected without sacrificing fiber properties (i.e., length) to a significant degree. The ramifications of this development are wide. Can yarn be made after attenuation and alignment? Another embodiment of this system is the use of it to align webs for composite applications.

While the development of the drafting system was taking place, an effort to characterize the pre-oxidized mat fibers was implemented. Fiber length distributions, strengths and elongation to break were determined for sixteen sample fibers supplied by Union Carbide. The fibers were then characterized after processing to determine the effect of processing on fiber properties. As discussed in the text of this report, it is clear that certain processing conditions indeed manifest superior results.

The original concept of this project was to develop a twistless bonded yarn. This was suggested since it appeared that the pre-oxidized fiber would not be able to withstand the harsh material-machine interactions imposed during twisting. However, after a preliminary feasibility study it appears that conventional twisting would be adequate for pre-oxidized pitch fibers.

Some of the problems encountered over the last six months include web uniformity. However, a method of doubling to improve uniformity

has been developed and will be implemented soon. Incoming web thickness is also a problem and a web splitting device is being developed which will automatically and continually reduce the web thickness prior to attenuation and alignment.

During the remainder of this contract, the following will be investigated:

1. Methods of Spinning
2. Web Uniformity
3. Web Thickness
4. Possibility of fabricating undirectional fibrous webs for composite fabrication.

LIST OF FIGURES

LIST OF FIGURES (cont.)

LIST OF TABLES

Project A-1912 Interim Report

October 12, 1976--March 31, 1977

"Processing of Pitch-Based Carbon Fiber into Yarn"

I. INTRODUCTION

As a result of discussions between the Carbon Fiber Development Laboratory of Union Carbide's Parma Technical Center and Georgia Institute of Technology, this program was initiated to determine the feasibility of spinning a staple carbon filament into a yarn capable of being woven into a fabric. The initial concept was to separate and align the carbon fibers and then form them into a parallel assembly which would be held together with a suitable resin system.

Concurrently, with the development of equipment, a test program was to be conducted to characterize sample mats and fibers with the objective of relating these properties to their ability to be processed into yarn.

II. TECHNICAL WORK

a) Mechanical System

The initial concept was to feed the mat through two soft rubber rolls onto a vacuum roll. The vacuum roll would be driven at a surface speed five to ten times the surface speed of the feed rolls. The web would then be transfered to another vacuum roll which feeds a moving knitted belt which would consolidate the fibers for resin additions. Figure 1 illustrates schematically this concept. After construction and initial trials, it was evident that several modifications were needed. However, the mat was successfully fed through the feed rolls without apparent damage. The addition of nips to the feed

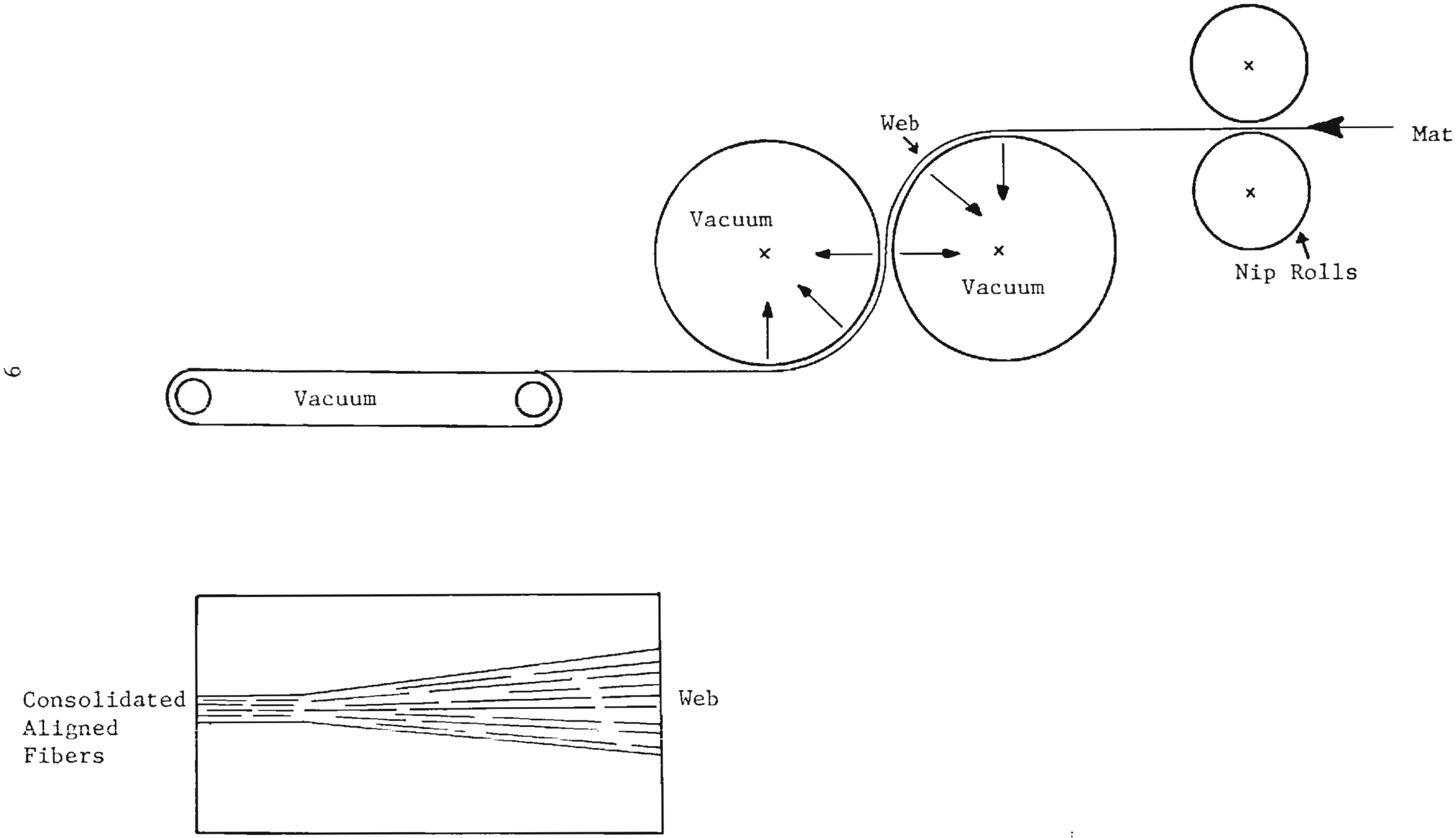


Figure 1. Initial Design of Machine to Align and Attenuate Staple Carbon Fibers

rolls to feed the first vacuum roll resulted in considerable improvement in operation of the equipment with some definite alignment and separation of fibers. It was noted that while a fairly high vacuum was applied to the vacuum roll, the fibers were not tightly held which resulted in poor and uneven webs. To solve this problem a very flexible plastic belt was installed to run over the top of the roll. The result was the carbon fibers were held tightly between the plastic and the roll by the suction force upon the film which greatly increased the area effected by the vacuum on the roll. A diagram of this system is shown in Figure 2. The results were extremely encouraging. Good fiber alignment and separation of the mat was achieved and significant consolidation was observed using the cloth belt table. However, the second vacuum roll proved to be unnecessary and was therefore removed from the system.

It was also noted that the aligned web coming from the first vacuum roll could be twisted by hand into short lengths of yarn. A mechanical system to spin and wind-up yarn continuously was designed and constructed. Primarily because of the difficulty in keeping the winding diameter constant; this approach has been temporarily abandoned in favor of a simpler system of spinning approximately three feet of yarn for test purposes. This system worked so well that the emphasis in the program was changed from the twistless bonded approach to a more conventional twisted yarn approach.

Many lengths of yarn were made and a small mat was hand woven from this yarn. While the yarn produced was not extremely uniform, it does demonstrate the feasibility of producing a yarn from staple

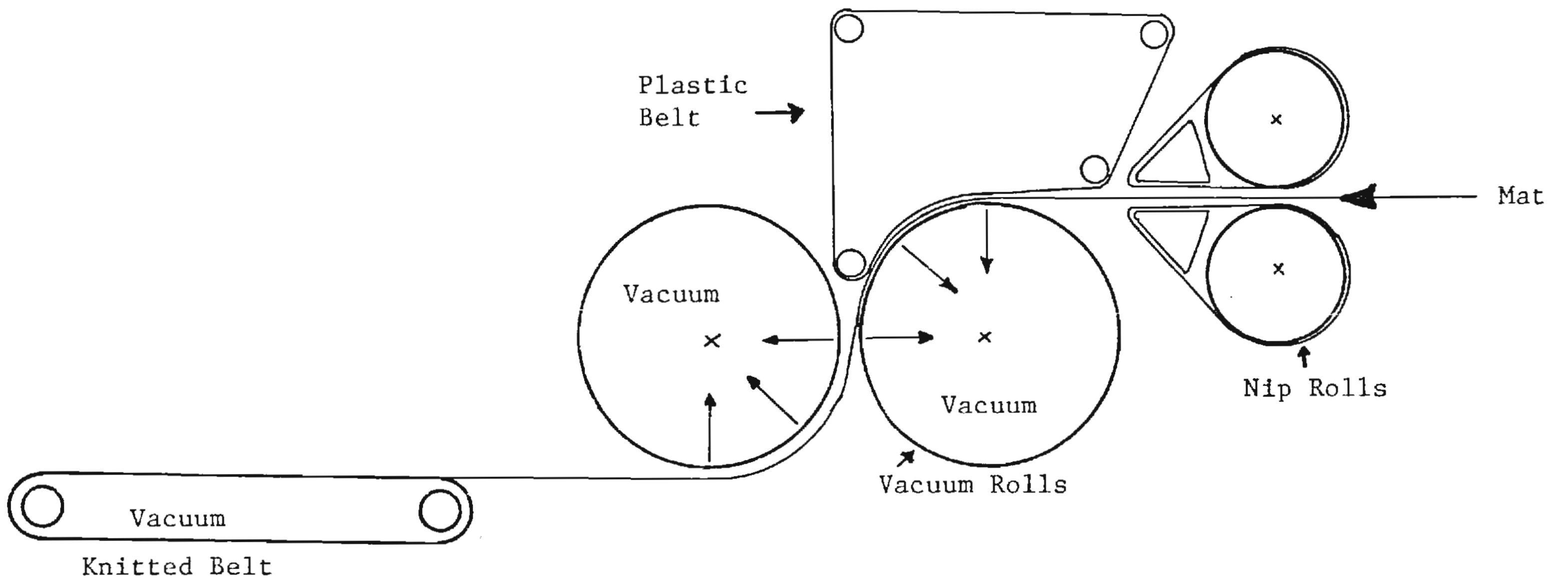


Figure 2. First Modification of System to
Align and Staple Carbon Fibers

carbon fibers. Figure 3 shows the final machine configuration which was used to spin the yarn samples.

As a result of this demonstration of feasibility, two areas of investigation are being actively pursued:

1. improvement of the uniformity of the web
2. investigation of alternate spinning methods.

The approach to improving the uniformity of the web is to average the thick and thin areas by doubling. To this end an additional drafting system has been designed and is now being fabricated.

The other spinning methods being investigated are:

1. Ring Spinning
2. Open Cup Spinning
3. Twistless Spinning
4. DREF Spinning.

Ring Spinning is illustrated in Figure 4. After the fibers are aligned they are twisted and wound on a bobbin by this process. In this process a traveler running on a ring mounted concentrically with a spindle causes the yarn balloon to lag the spindle thereby causing the yarn to wind continuously onto the bobbin and put twist in the yarn.

Open Cup Spinning is schematically shown in Figure 5A. In this process, the twisting and winding operations are separated. Twist is imparted by a spinning cup and the resultant yarn is would on a bobbin. Twistless Spinning is illustrated in Figure 5B.

The final process called DREF Spinning is shown in Figure 6. In this process the aligned web is directly rolled into a yarn as shown in the sketch.

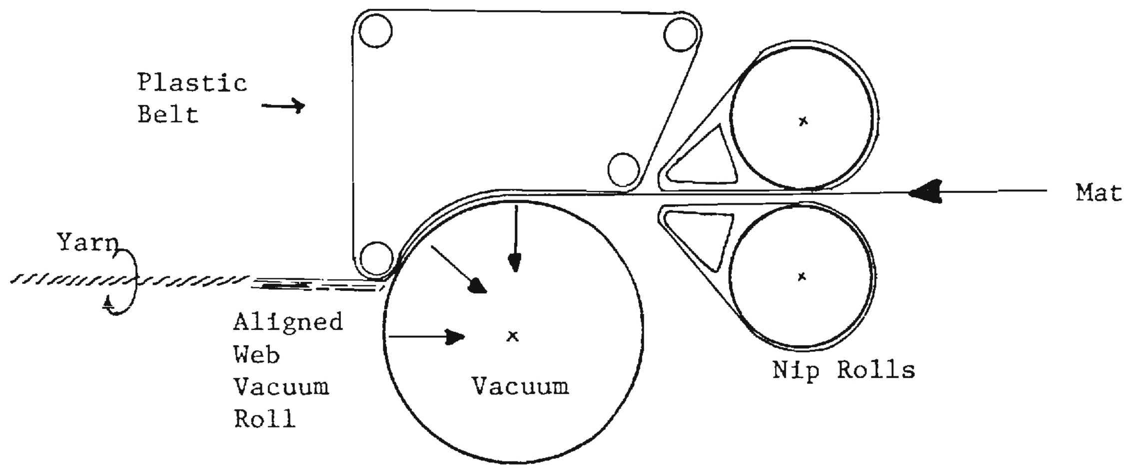


Figure 3. Final Machine Configuration for Making Yarn Samples

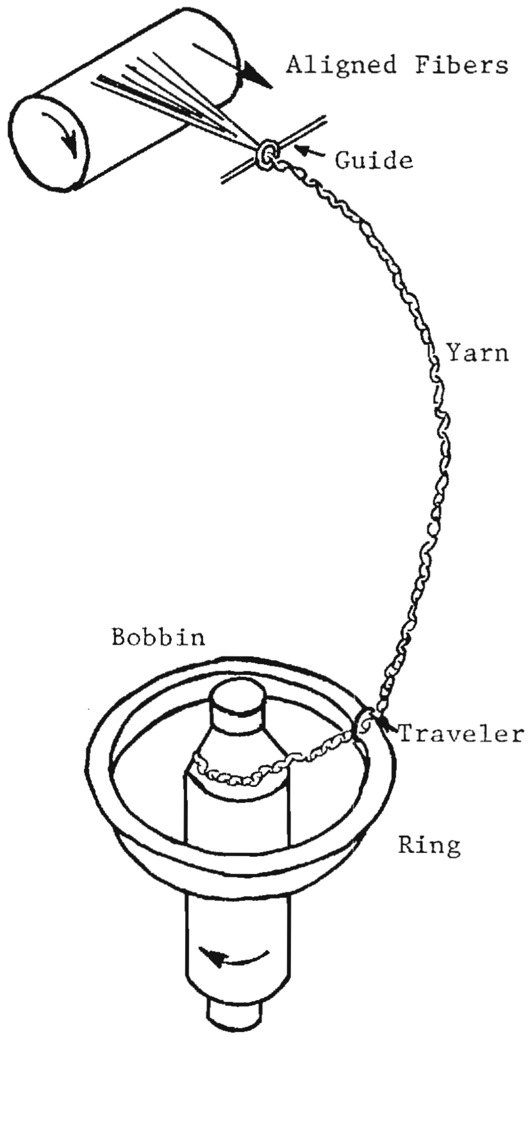


Figure 4. Schematic of Ring Spinning System

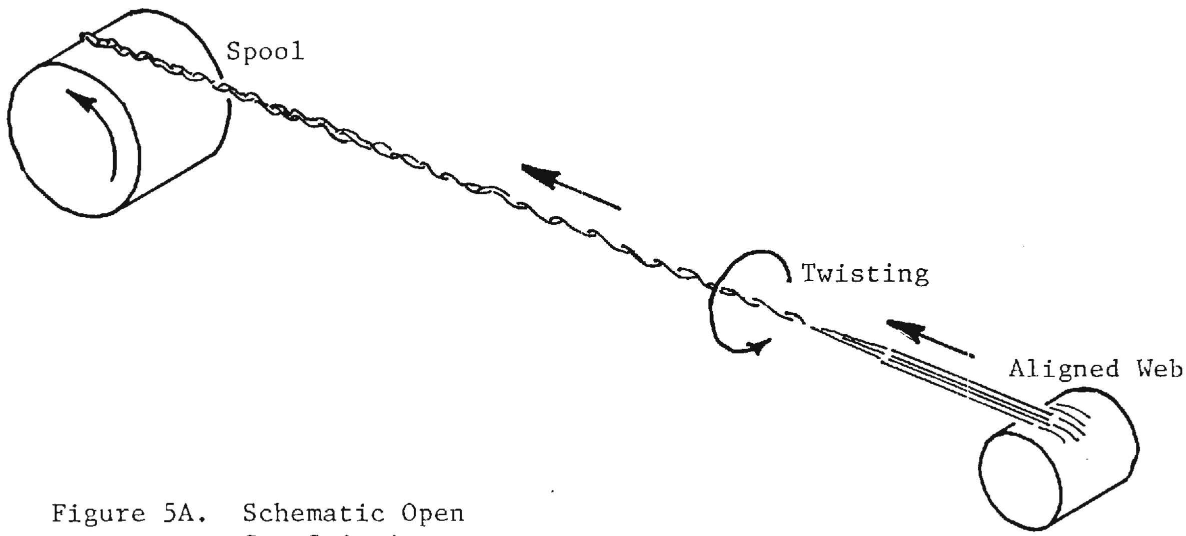


Figure 5A. Schematic Open Cup Spinning

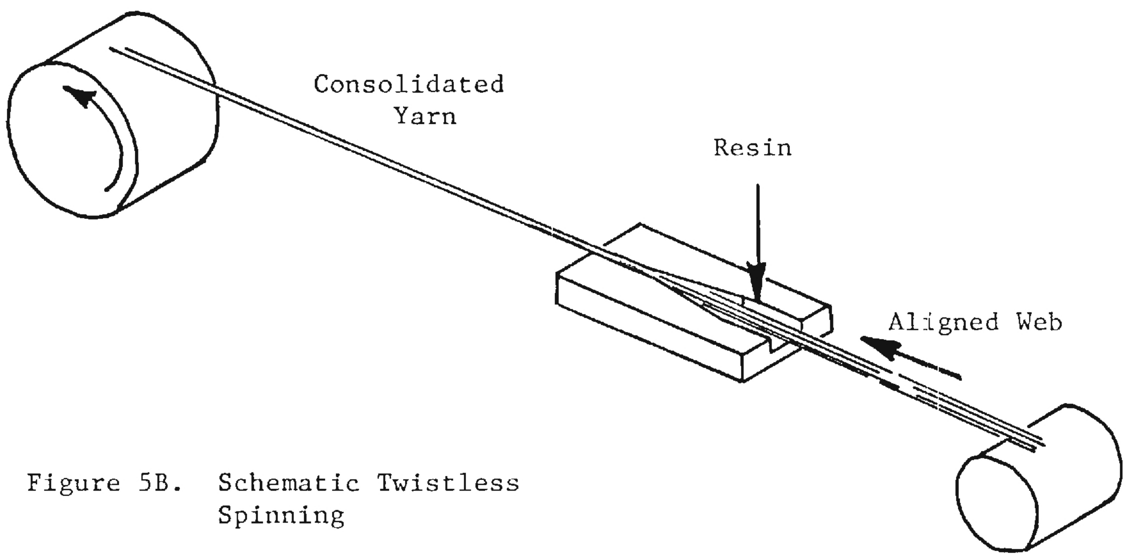


Figure 5B. Schematic Twistless Spinning

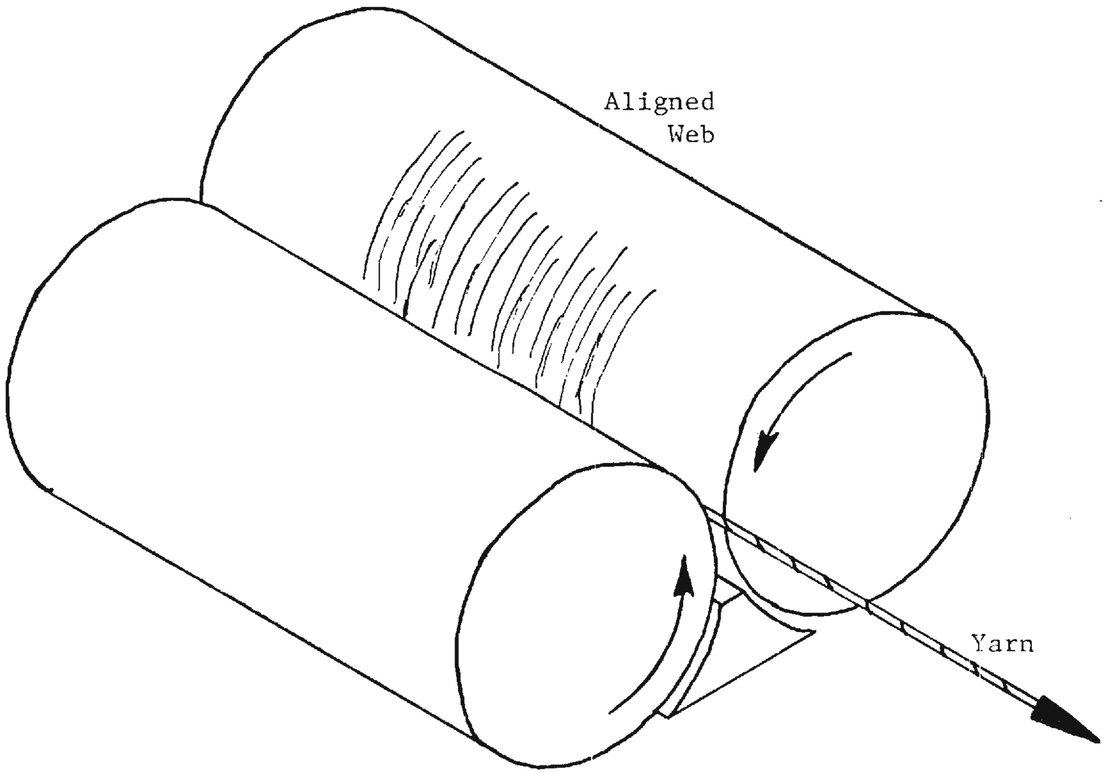


Figure 6. Schematic of DREF Spinning

b) Material-Machine Interaction

The primary objective of the drafting process which must occur prior to manufacturing yarn is to attenuate and align the preoxidized fibers without significantly damaging them in the process. Since these fibers are relatively brittle, they cannot be subjected to machine interactions which produce severe treatment. Accordingly, the fibers cannot be gripped too harshly by the roll nip nor can they be subjected to severe deformations. The drafting system described in Section II(a) was designed and developed to align and attenuate the fibers. The alignment and attenuation is affected by gripping the fibers at one end and pulling them on the other end. This is accomplished by having the processing surfaces move at different speeds relative to each other. That is, the lead surface is going from about five to ten times faster than the trailing surface. Accordingly, if a mat of a given thickness is processed through the system and the surface speed ratio is five, the resulting thickness will be one fifth (1/5) that of the original.

There are several problems which can occur with a drafting system of this type. For one, it is extremely critical that the gripping force is powerful enough to hold the fibers without inadvertantly crushing them. Experience has indicated that the rollers must be soft and rubbery to meet this requirement. At one time a hard conventional roller was employed and the fibers were simply pulverized. Also it is critical that the gripping surface of the lead drafting surface be sufficient to affect drafting. That is, the fibers must be extracted uniformly from the trail nip rollers. This all must be accomplished without breaking the fibers.

In order to determine the efficiency of the developed drafting system, a series of tests were made in which the fiber length distributions at different porcessing parameters were measured before and after drafting. Figure 7 provides the fiber length distributions prior to processing. The average fiber length was 3.56 cm; however, the range of lengths was indeed widespread. The modal length was between 3.0 and 4.0 centimeters. Processing parameters included five different draft ratios (i.e., 5, 10, 15, 20, 25). For a draft ratio of 5, three different speed combinations were employed and two were employed for a draft ratio of 10. Figures 8 through 18 provide the length distributions combinations. It is clearly evident that the drafting system damages fibers greater than 5 cm for all processing combinations. The reduction of length could be prevented by increasing the distance between the nip roller and the vacuum roller, but this might only serve to increase the nonuniformity of the fibrous web.

Figure 19 provides a summary of the effect of processing on fiber length. Upon observation of this data one can conclude that the drafting system is quite efficient with regard to preserving fiber length.

To determine the effect of processing on alignment and attenuation, photomicrographs were taken of the mat before and after drafting. Figure 20 provides a set of before and after pictures for a draft ratio of 5 where the nip roller is proceeding at .21 cm/sec and the vacuum roller is proceeding at 1.05 cm/sec. Inspection of these pictures clearly indicates the degree of alignment after processing.

After alignment, it is interesting to note the small bits of

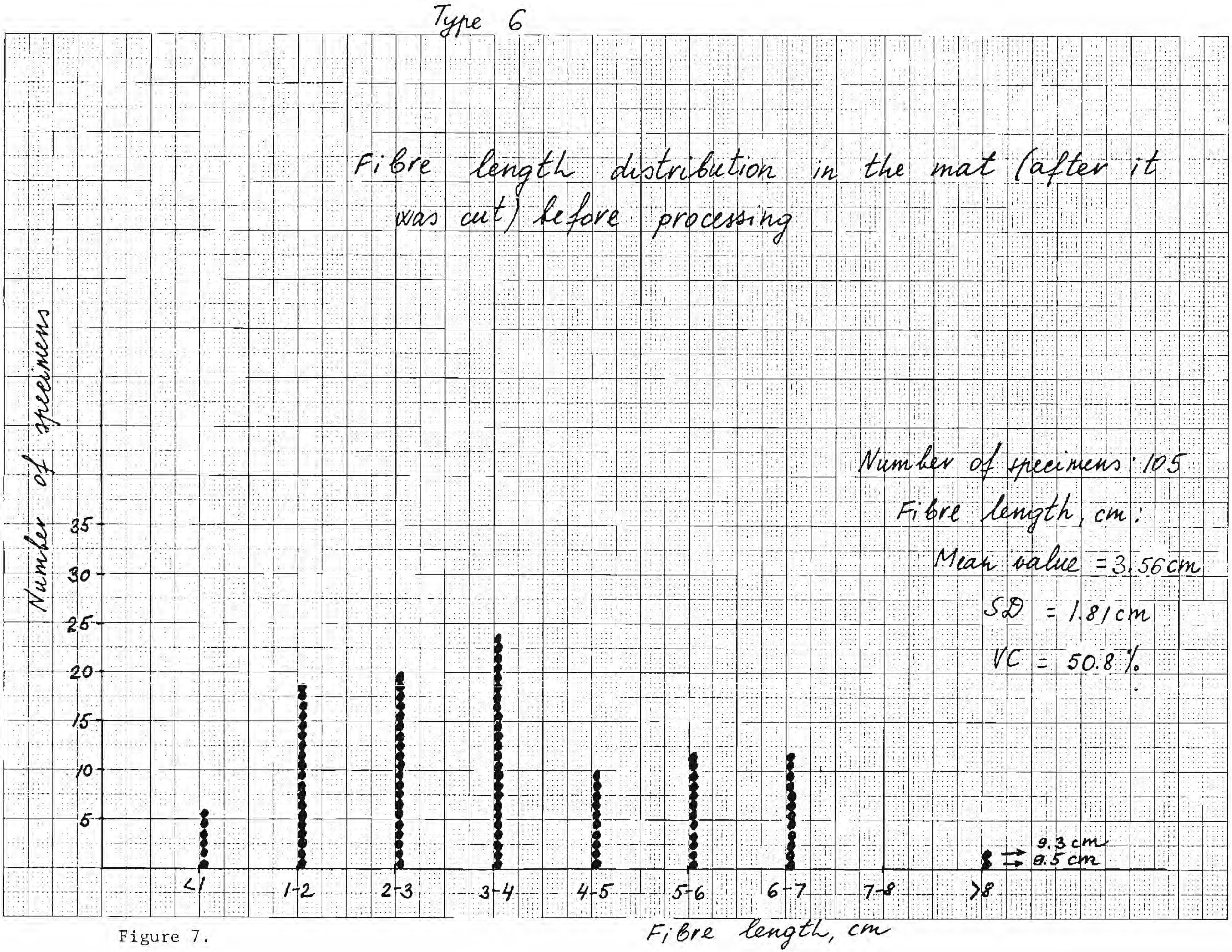

Type 6
Fibre length distribution in the mat (after it was cut) before processing
Number of specimens: 105
Fibre length, cm:
Mean value = 3.56 cm
SD = 1.81 cm
VC = 50.8 %
9.3 cm
8.5 cm
Number of specimens
35
30
25
20
15
10
5
<1
1-2
2-3
3-4
4-5
5-6
6-7
7-8
>8
Fibre length, cm

Figure 7.

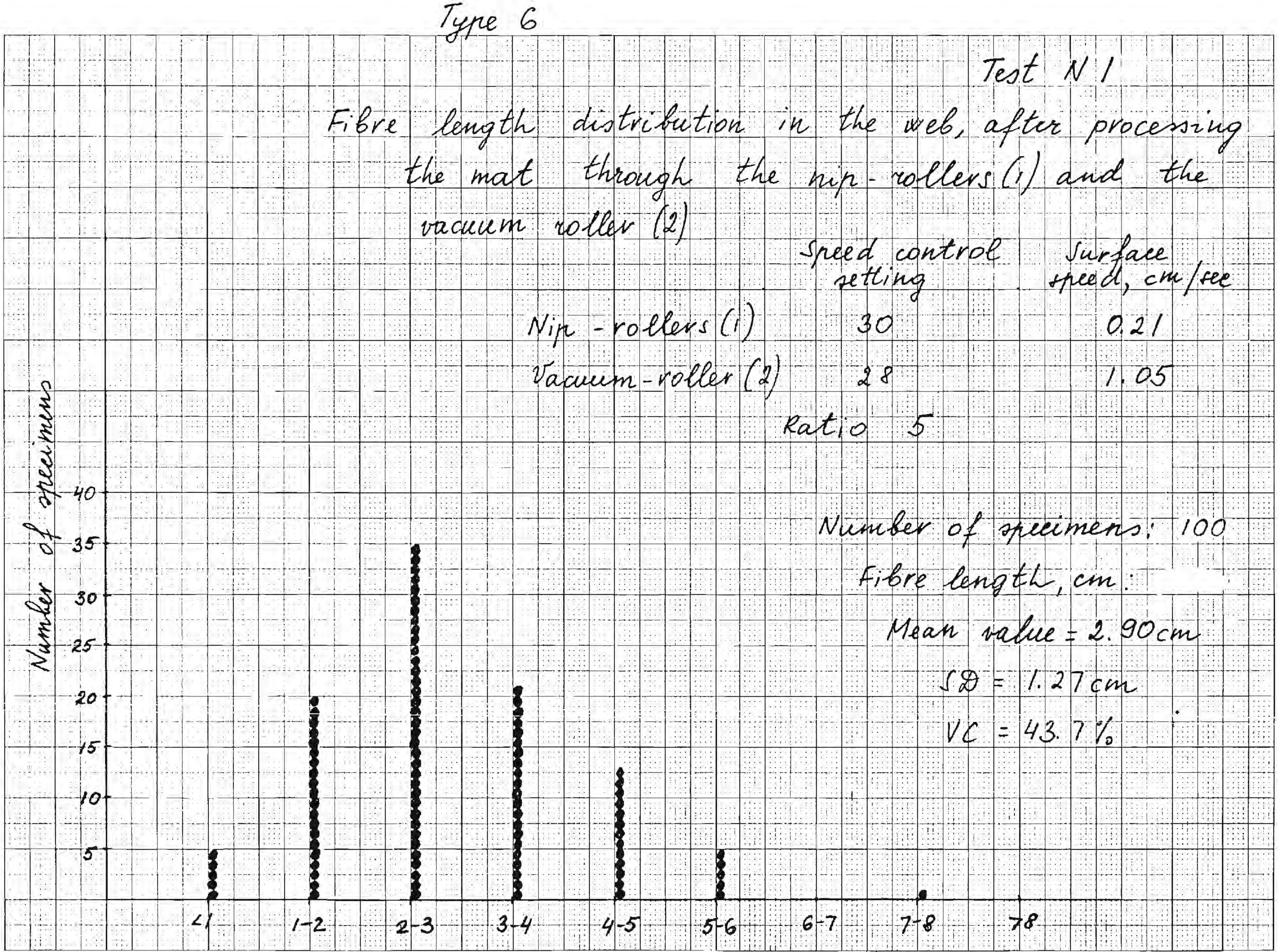

Type 6
Test N 1
Fibre length distribution in the web, after processing the mat through the nip-rollers (1) and the vacuum roller (2)
Speed control setting
Surface speed, cm/sec
Nip-rollers (1) 30 0.21
Vacuum-roller (2) 28 1.05
Ratio 5
Number of specimens: 100
Fibre length, cm:
Mean value = 2.90 cm
SD = 1.27 cm
VC = 43.7%
Number of specimens
40
35
30
25
20
15
10
5
<1
1-2
2-3
3-4
4-5
5-6
6-7
7-8
>8
Fibre length, cm

Figure 8.

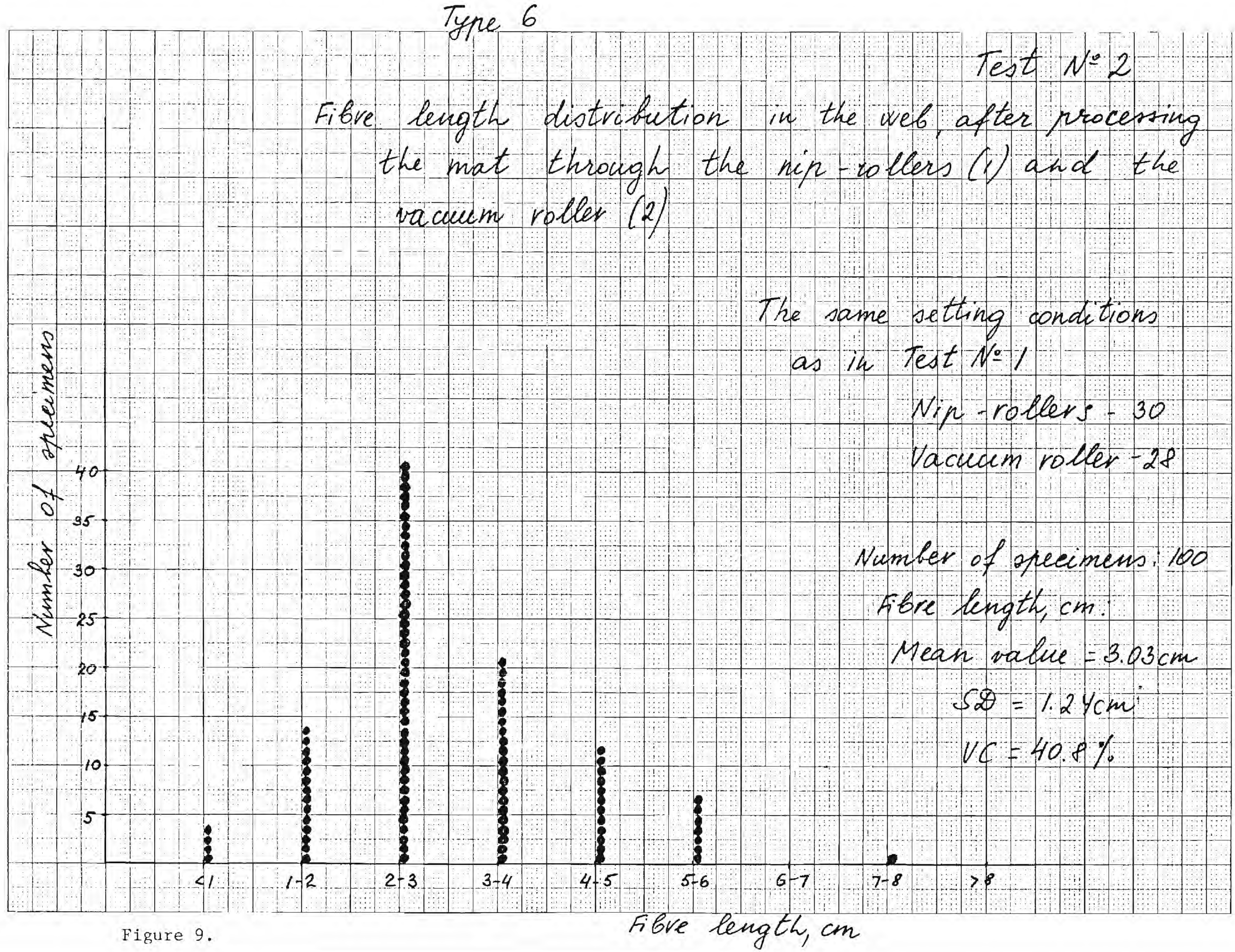

Type 6
Test № 2
Fibre length distribution in the web, after processing the mat through the nip-rollers (1) and the vacuum roller (2)
The same setting conditions as in Test № 1
Nip-rollers - 30
Vacuum roller - 28
Number of specimens: 100
Fibre length, cm.
Mean value = 3.03cm
SD = 1.24cm
VC = 40.8%
Number of specimens
40
35
30
25
20
15
10
5
<1
1-2
2-3
3-4
4-5
5-6
6-7
7-8
>8
Fibre length, cm

Figure 9.

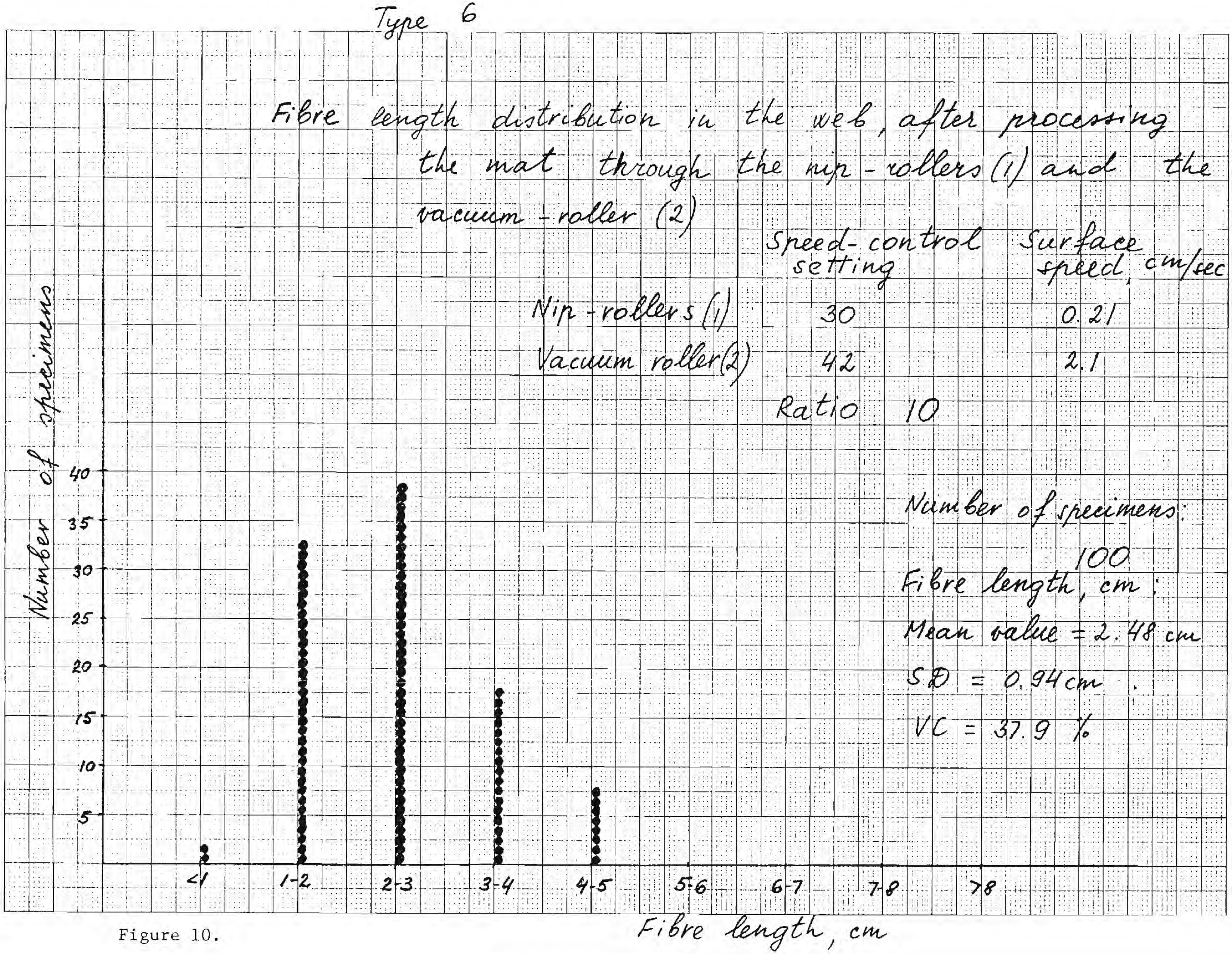

Type 6
Fibre length distribution in the web, after processing the mat through the nip-rollers (1) and the vacuum-roller (2)
Speed-control setting
Surface speed, cm/sec
Nip-rollers (1) 30 0.21
Vacuum roller (2) 42 2.1
Ratio 10
Number of specimens: 100
Fibre length, cm:
Mean value = 2.48 cm
SD = 0.94 cm.
VC = 37.9 %
Number of specimens
40
35
30
25
20
15
10
5
<1
1-2
2-3
3-4
4-5
5-6
6-7
7-8
>8
Fibre length, cm

Figure 10.

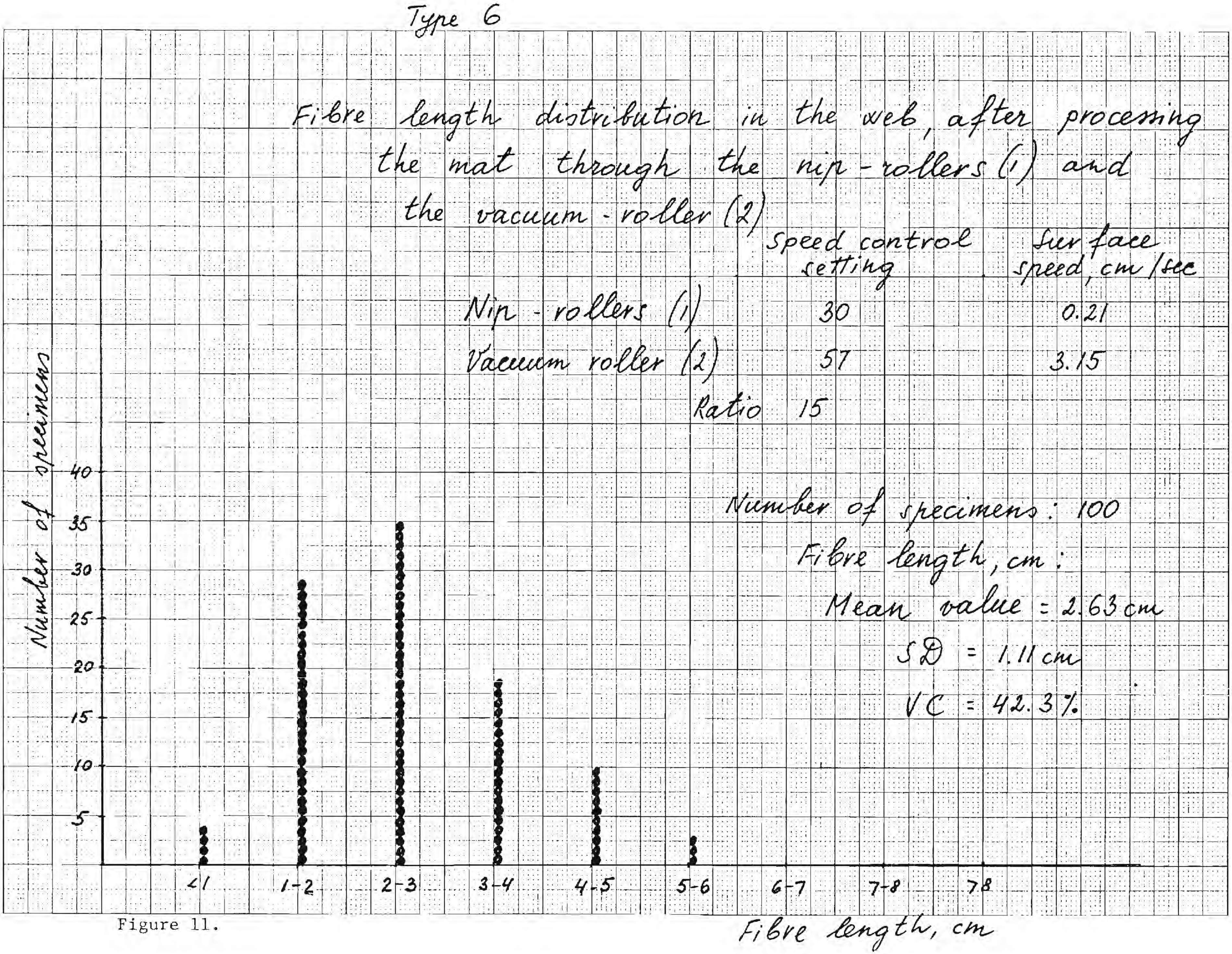

Type 6
Fibre length distribution in the web, after processing the mat through the nip-rollers (1) and the vacuum-roller (2)
Speed control setting
Surface speed, cm/sec
Nip-rollers (1) 30 0.21
Vacuum roller (2) 57 3.15
Ratio 15
Number of specimens: 100
Fibre length, cm:
Mean value = 2.63 cm
SD = 1.11 cm
VC = 42.3%
Number of specimens
40
35
30
25
20
15
10
5
<1
1-2
2-3
3-4
4-5
5-6
6-7
7-8
>8
Fibre length, cm

Figure 11.

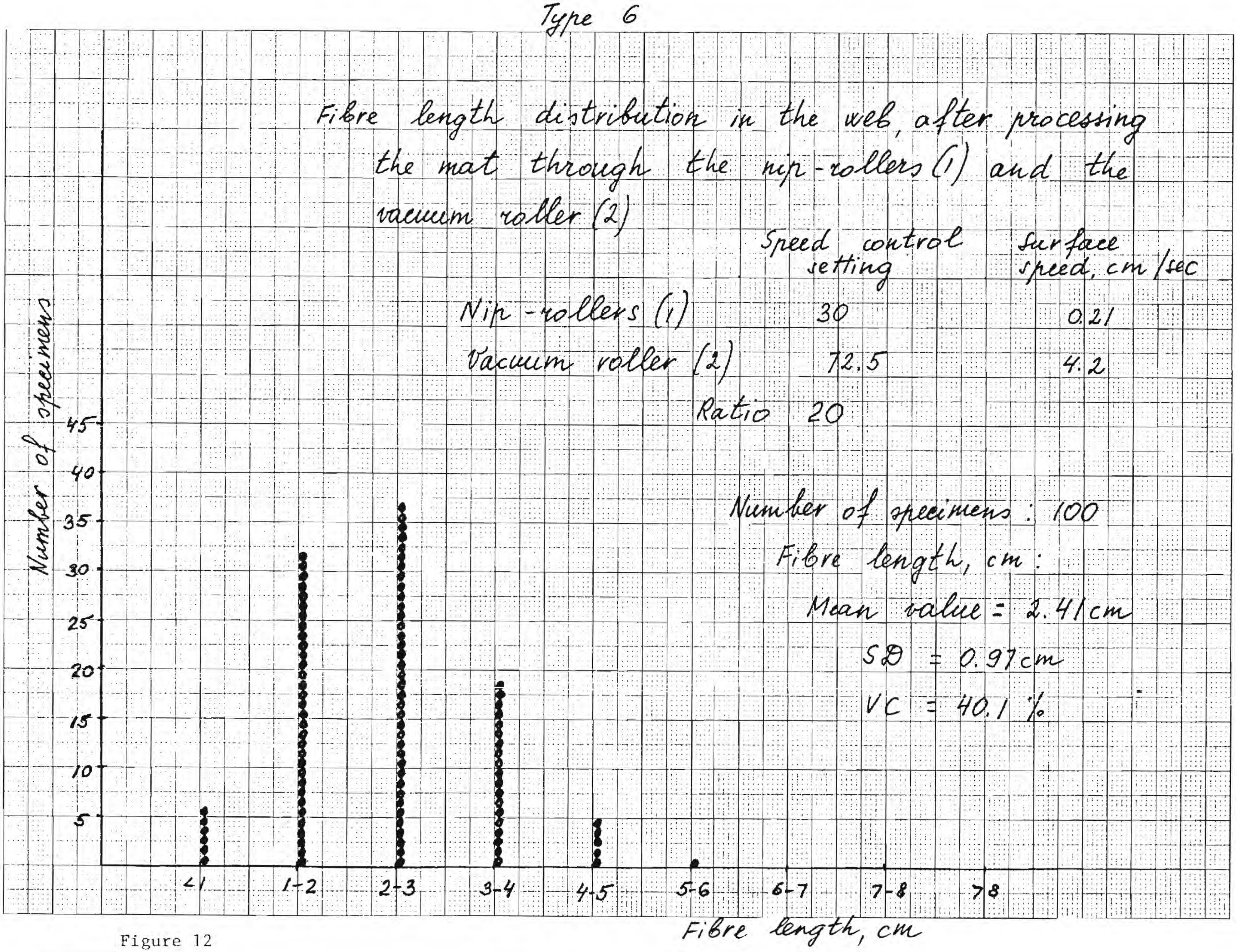

Type 6
Fibre length distribution in the web, after processing the mat through the nip-rollers (1) and the vacuum roller (2)
Speed control setting
Surface speed, cm/sec
Nip-rollers (1) 30 0.21
Vacuum roller (2) 72.5 4.2
Ratio 20
Number of specimens : 100
Fibre length, cm :
Mean value = 2.41 cm
SD = 0.97 cm
VC = 40.1 %
Number of specimens
45
40
35
30
25
20
15
10
5
<1
1-2
2-3
3-4
4-5
5-6
6-7
7-8
>8
Fibre length, cm

Figure 12

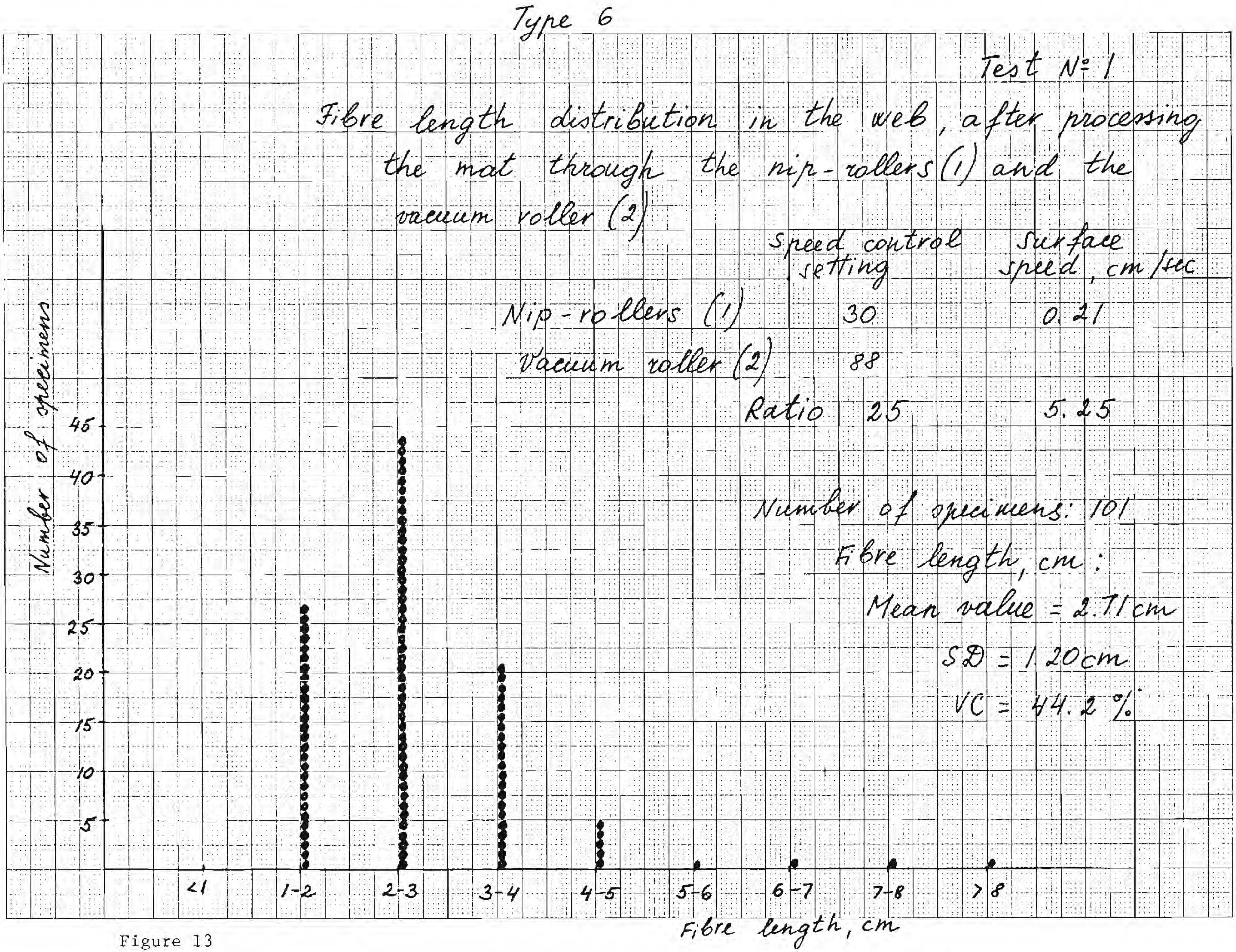

Type 6
Test N° 1
Fibre length distribution in the web, after processing the mat through the nip-rollers (1) and the vacuum roller (2)
Speed control setting
Surface speed, cm/sec
Nip-rollers (1) 30 0.21
Vacuum roller (2) 88
Ratio 25 5.25
Number of specimens: 101
Fibre length, cm:
Mean value = 2.71 cm
SD = 1.20 cm
VC = 44.2 %
Number of specimens
45
40
35
30
25
20
15
10
5
<1
1-2
2-3
3-4
4-5
5-6
6-7
7-8
>8
Fibre length, cm

Figure 13

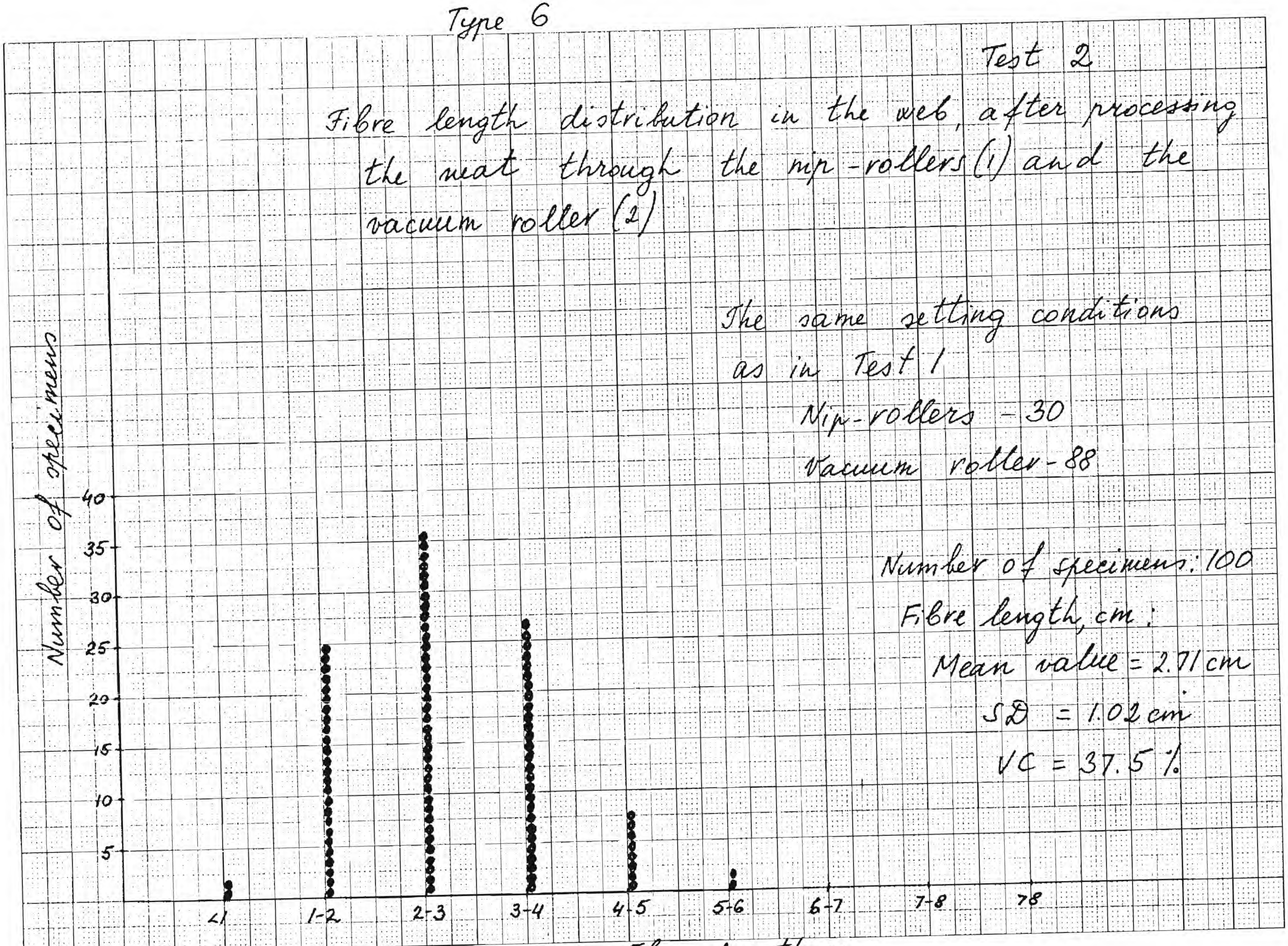

Type 6
Test 2
Fibre length distribution in the web, after processing the mat through the nip-rollers (1) and the vacuum roller (2)
The same setting conditions as in Test 1
Nip-rollers - 30
Vacuum roller - 88
Number of specimens: 100
Fibre length, cm:
Mean value = 2.71 cm
SD = 1.02 cm
VC = 37.5 %
Number of specimens
40
35
30
25
20
15
10
5
<1
1-2
2-3
3-4
4-5
5-6
6-7
7-8
78
Fibre length, cm

Figure 14

Type 6

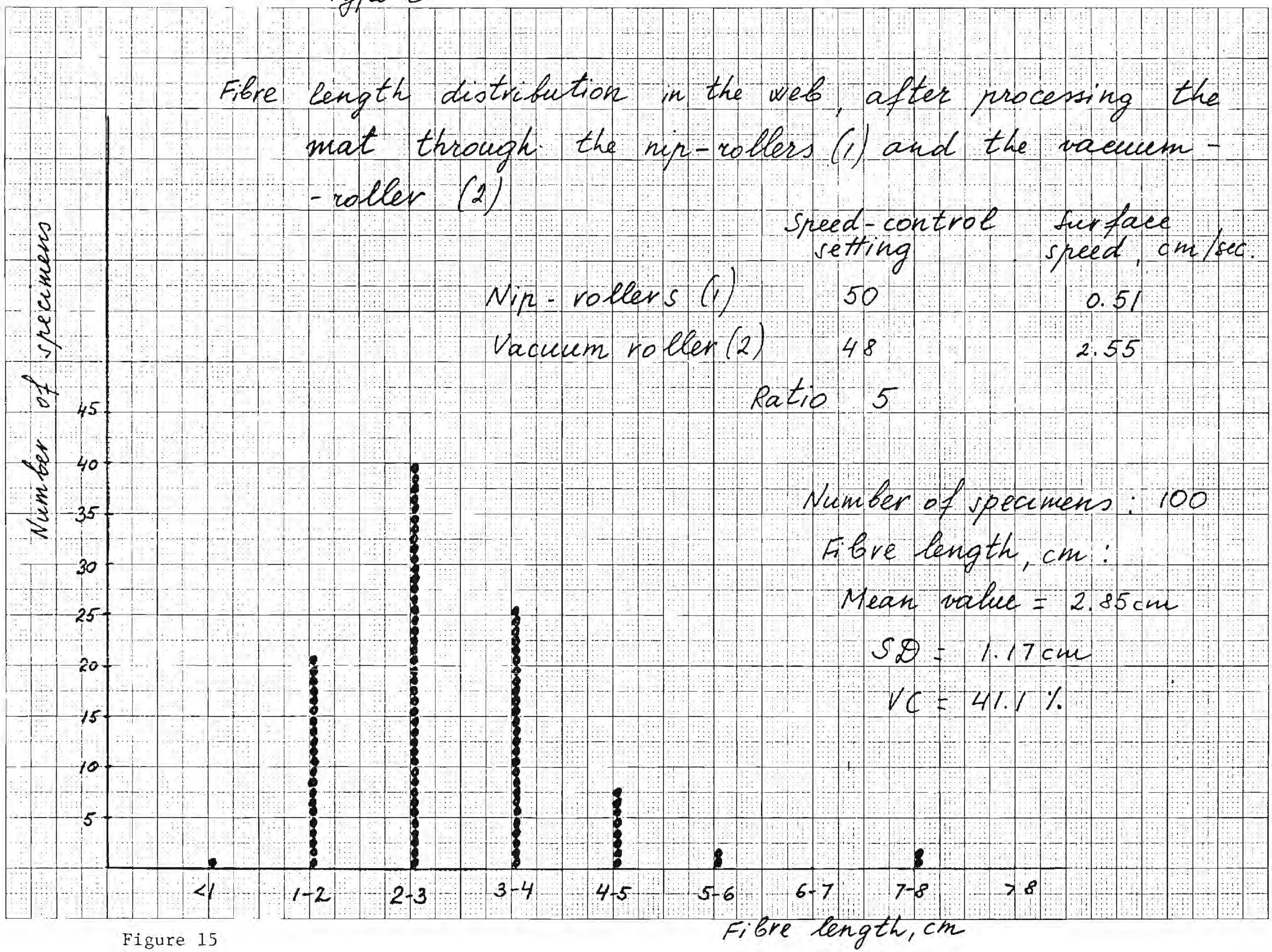


Figure 15

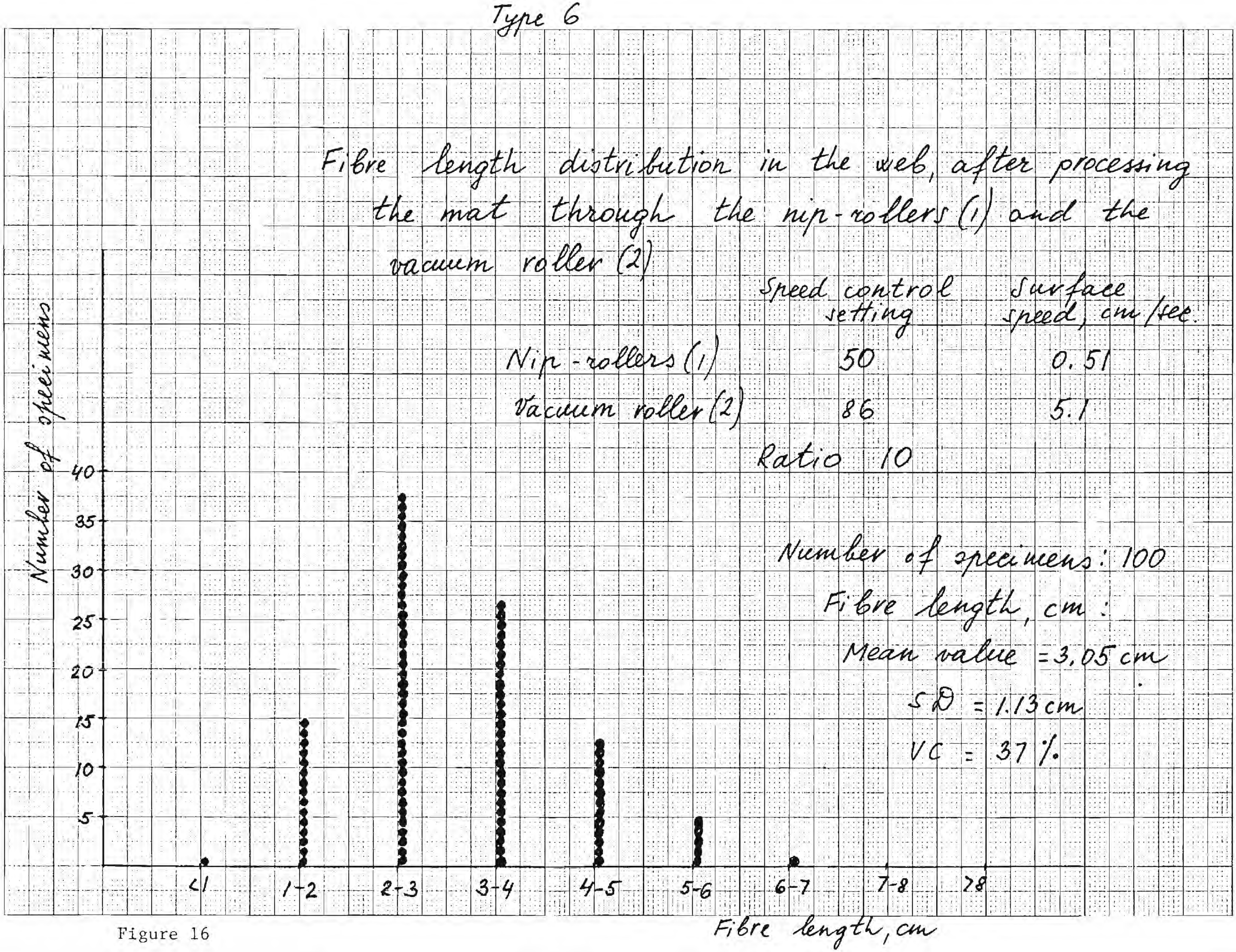

Type 6
Fibre length distribution in the web, after processing the mat through the nip-rollers (1) and the vacuum roller (2)
Speed control setting
Surface speed, cm/sec.
Nip-rollers (1) 50 0.51
Vacuum roller (2) 86 5.1
Ratio 10
Number of specimens: 100
Fibre length, cm:
Mean value = 3.05 cm
SD = 1.13 cm
VC = 37 %
Number of specimens
40
35
30
25
20
15
10
5
<1
1-2
2-3
3-4
4-5
5-6
6-7
7-8
>8
Fibre length, cm

Figure 16

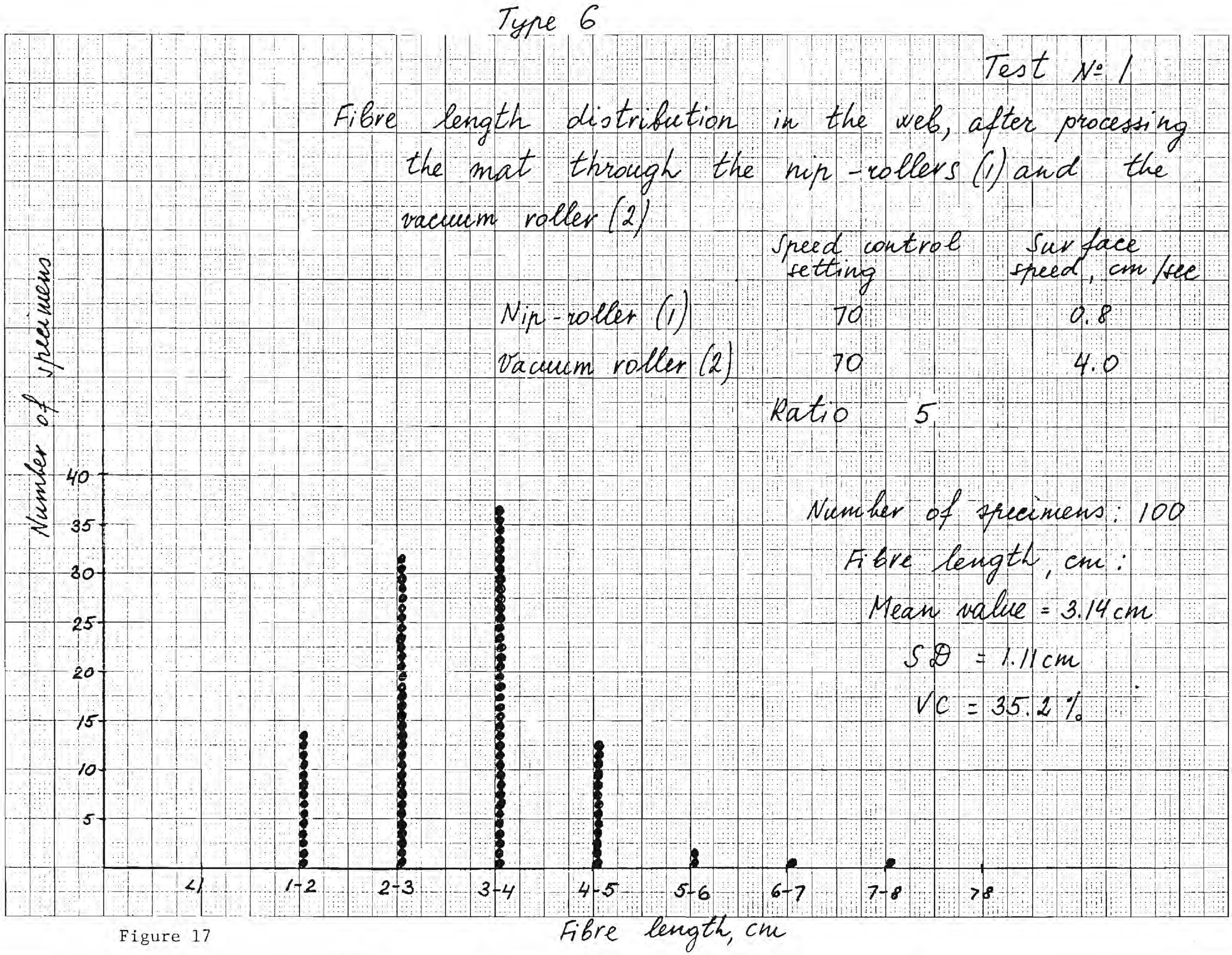

Type 6
Test № 1
Fibre length distribution in the web, after processing the mat through the nip-rollers (1) and the vacuum roller (2)
Speed control setting
Surface speed, cm/sec
Nip-roller (1) 70 0.8
Vacuum roller (2) 70 4.0
Ratio 5
Number of specimens: 100
Fibre length, cm:
Mean value = 3.14 cm
SD = 1.11 cm
VC = 35.2 %
Number of specimens
40
35
30
25
20
15
10
5
<1
1-2
2-3
3-4
4-5
5-6
6-7
7-8
>8
Fibre length, cm

Figure 17

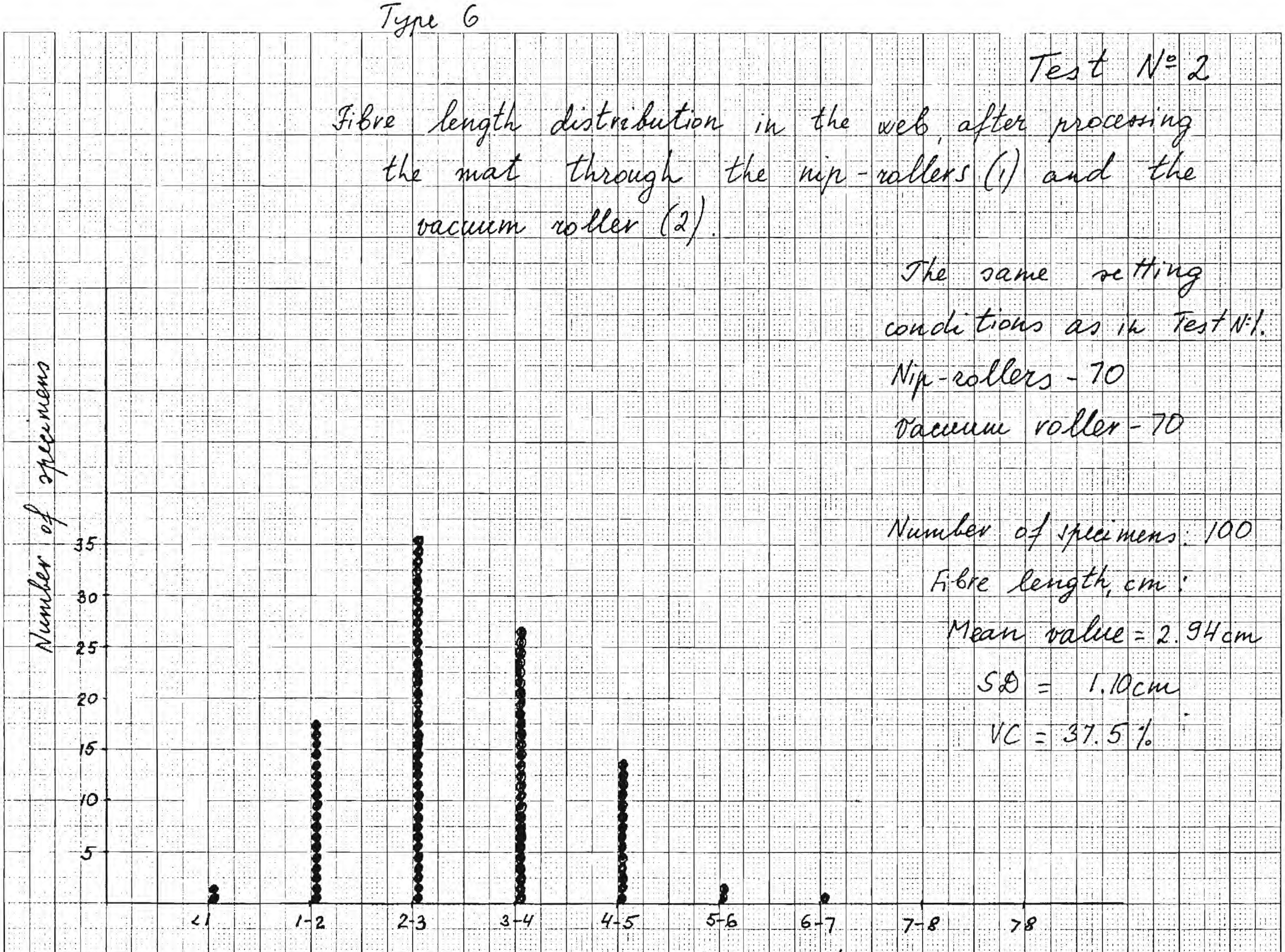

Type 6
Test № 2
Fibre length distribution in the web, after processing the mat through the nip-rollers (1) and the vacuum roller (2).
The same setting conditions as in Test №1.
Nip-rollers - 70
Vacuum roller - 70
Number of specimens: 100
Fibre length, cm:
Mean value = 2.94 cm
SD = 1.10 cm
VC = 37.5 %
Number of specimens
35
30
25
20
15
10
5
<1
1-2
2-3
3-4
4-5
5-6
6-7
7-8
>8
Fibre length, cm

Figure 18

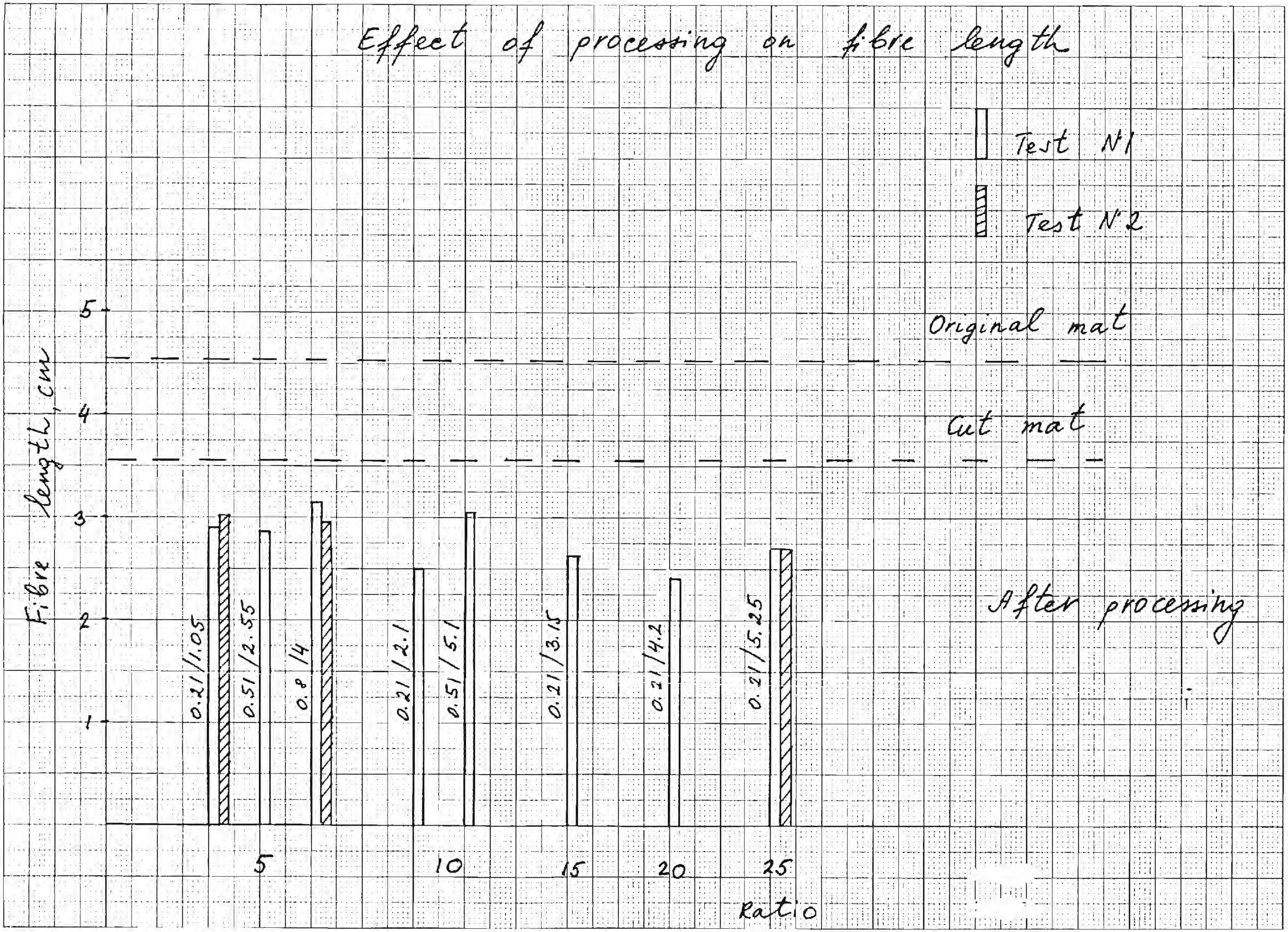
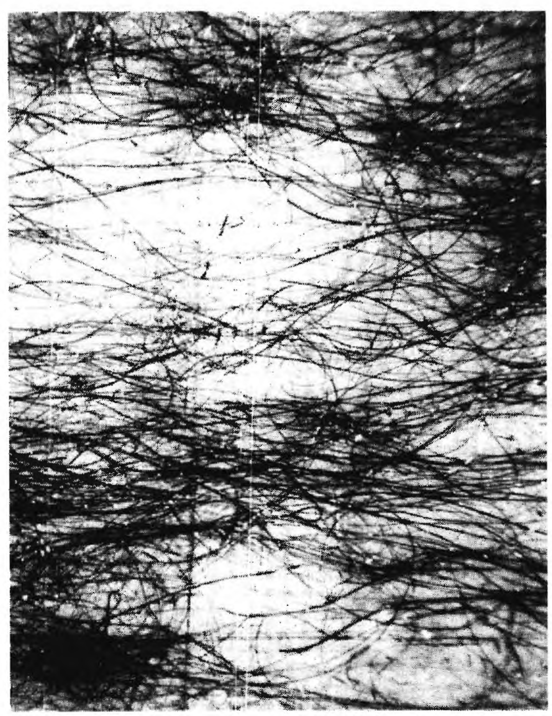

Effect of processing on fibre length
Test N°1
Test N°2
Original mat
Cut mat
After processing
Fibre length, cm
5
4
3
2
1
0.21/1.05
0.51/2.55
0.8/4
0.21/2.1
0.51/5.1
0.21/3.15
0.21/4.2
0.21/5.25
5
10
15
20
25
Ratio

Figure 19

Figure 20--Fibers Before and After Drafting

BEFORE



AFTER

fibers which manifest in the web. These are probably small pieces of fibers which were greater than 5 cm prior to processing.

Inspection of the mat after processing indicates that its linear uniformity might be a candidate for improvement. Accordingly, a task has been assigned to develop a second drafting unit. This unit will be employed to provide a second aligned web. As is common in most textile processing, this web will be combined or doubled with the first web. Accordingly, the thick and thin spots forming both webs should cancel out and a new uniformed combined web should result. This effort, as it unfolds, will be provided in a later report.

c) Characterization of Sample Mats and Fibers

Samples were taken from the carbon fiber mats as received. Diameters and lengths of about 100 fibers were measured. The mean diameter and length, the standard deviations, and the aspect ratios for these fibers were calculated. This data is presented in Table I.

Using an Instron testing machine, single fiber samples from selected mats were tested to determine textile strength and Young's modulus. This data is shown in Table II.

Fiber-fiber friction properties were determined upon selected single filament samples. Typical results of these tests are shown in Figures 21, 22, 23. These Figures show the friction force as a function distance along the fiber under normal forces of 1 mg, 5 mg and 10 mg. The large peaks in friction might be due to the characteristic variation in diameter of the fiber along its axis.

TABLE I.

Dimensional Properties of Carbon Fibers

No.	Type	Diameter, Mean,	SD,	VC, %	Length, cm Mean, cm	SD, cm	VC, %	Aspect Ratio
1	132	10.5	4.0	38.5	3.79	1.71	45.2	3609
2	133				3.14	1.66	52.7	2990
3	131				4.38	1.93	44.1	4171
4	120				2.54	1.18	46.6	2419
5	322	7.7	4.4	57.9	4.10	1.80	44.0	5324
6	323				4.69	1.89	40.2	6091
7	330				2.72	1.25	46.4	3532
8	321				4.69	2.04	43.6	6091
9	423	7.0	3.2	45.52	3.05	1.38	45.1	4357
10	422				3.95	1.78	45.1	5643
11	430				2.46	0.94	38.4	3514
12	421				3.66	1.79	49.0	5229
13	522	14.4	5.4	37.8	4.09	1.99	48.6	2840
14	530				2.71	1.17	43.1	1882
15	521				4.34	1.82	42.0	3014
16	6	11.7	4.6	39.1	4.54	2.04	45.0	3880

TABLE II. Fiber Tensile Data Tensile strength.

No.	Type	Diameter μm	Density g/cm^3	Linear density den(tex)	Breaking load, pounds (gf): Mean value, pounds(gf)	Breaking load: Standard deviation, pounds(gf)	Breaking load: Variation Coefficient %	Specific strength, psi (Tenacity gf/den): Mean value, psi(gf/den)	Specific strength: Standard deviation, psi(gf/den)	Specific strength: Variation Coefficient %	Breaking extension, %: Mean Value %	Breaking extension: Standard deviation, %	Breaking extension: Variation Coefficient %	Young modulus, psi (Tensile modulus, g/den)
1	132	10.5	1.35	1.05(0.11)	6.2X10^{-3} (2.82)	2.8X10^{-3}(1.26)	44.8	46321 (2.68)	20752 (1.20)	44.8	7.56	2.78	36.9	0.6X10^{6}(3.54)
2	133				6.3X10^{-3} (2.86)	2.3X10^{-3}(1.04)	36.4	46978 (2.71)	17100 (0.99)	36.4	2.83	0.79	28.6	1.7X10^{6}(95.8)
3	131				5.6X10^{-3} (2.56)	2.2X10^{-3}(1.00)	38.9	42050 (2.43)	16357 (0.95)	38.9	4.67	2.47	52.9	0.9X10^{6}(51.9)
4	120				Breaking load showed to be less than 0.5g									
5	322	7.7	1.35	0.57(0.06)	7.3X10^{-3} (3.31)	1.7X10^{-3}(0.79)	23.9	101100(5.85)	24163 (1.39)	23.9	2.94	0.79	26.9	3.4X10^{6}(198.8)
6	323				6.0X10^{-3} (2.71)	2.1X10^{-3}(0.97)	35.9	82774 (4.78)	29715 (1.72)	35.9	3.0	0.68	23.0	2.8X10^{6}(161.9)
7	330				Breaking load showed to be less than 0.5g									
8	321				6.2X10^{-3}(2.82)	2.0X10^{-3}(0.93)	33.0	86133 (4.97)	28424 (1.64)	33.0	2.78	0.68	24.1	3.1X10^{6}(178.9)
9	423	7.0	1.35	0.47(0.05)	3 X10^{-3}(1.35)	2.0X10^{-3}(0.89)	65.7	49893 (2.89)	32780	65.7	2.15	0.89	41.5	2.3X10^{6}(133.9)
10	422				5.2X10^{-3}(2.36)	2.6X10^{-3}(1.16)	49.2	87036 (5.03)	42822 (2.47)	49.2	2.98	0.94	31.0	2.9X10^{6}(168.7)
11	430				Breaking load showed to be less than 0.5g									
12	421				5.0X10^{-3}(2.27)	1.7X10^{-3}(0.79)	35.0	83821 (4.84)	29337 (1.69)	35.0	3.39	0.84	24.3	2.5X10^{6}(143.1)
13	522	14.4	1.35	1.98(0.02)	7.0X10^{-3}(3.18)	3.4X10^{-3}(1.53)	47.9	27772 (1.60)	13303 (0.83)	47.9	2.83	0.68	24.8	1.0X10^{6}(56.7)
14	530				Breaking load showed to be less than 0.5g									
15	521				6.5X10^{-3}(2.97)	2.6X10^{-3}(1.18)	39.6	25938 (1.49)	10271 (0.59)	39.6	2.99	0.63	21.7	0.9X10^{6}(50.2)
16	6	11.7	1.35	1.31(0.14)	6.3X10^{-3}(2.87)	2.7X10^{-3}(1.21)	42.31	37968 (2.19)	16060 (0.93)	42.3	3.2	1.21	37.92	1.2X10^{6}(68.5)

20 ~/in

Figure 21.

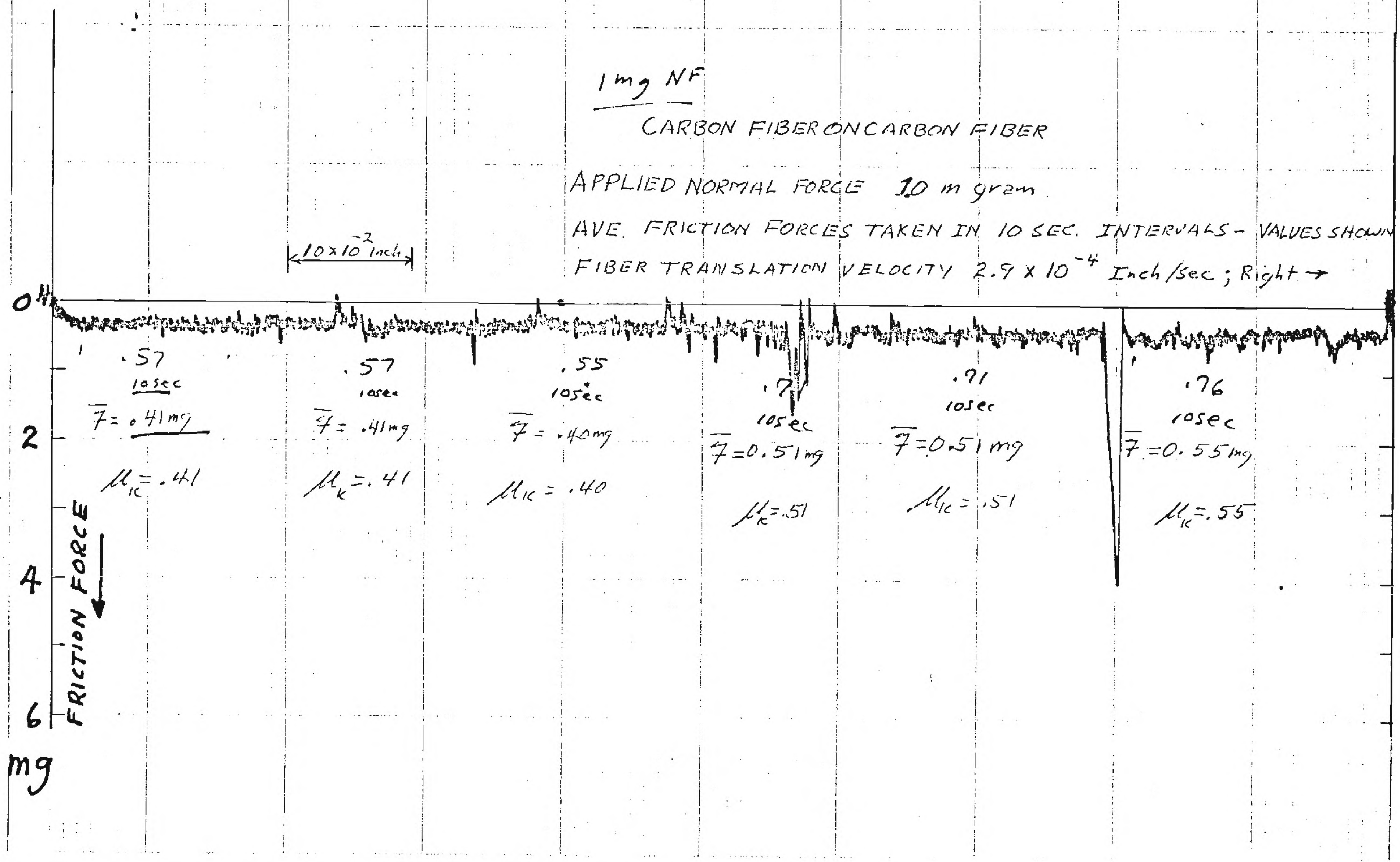


Figure 22.

5 mg NF

y @ 20 in/in

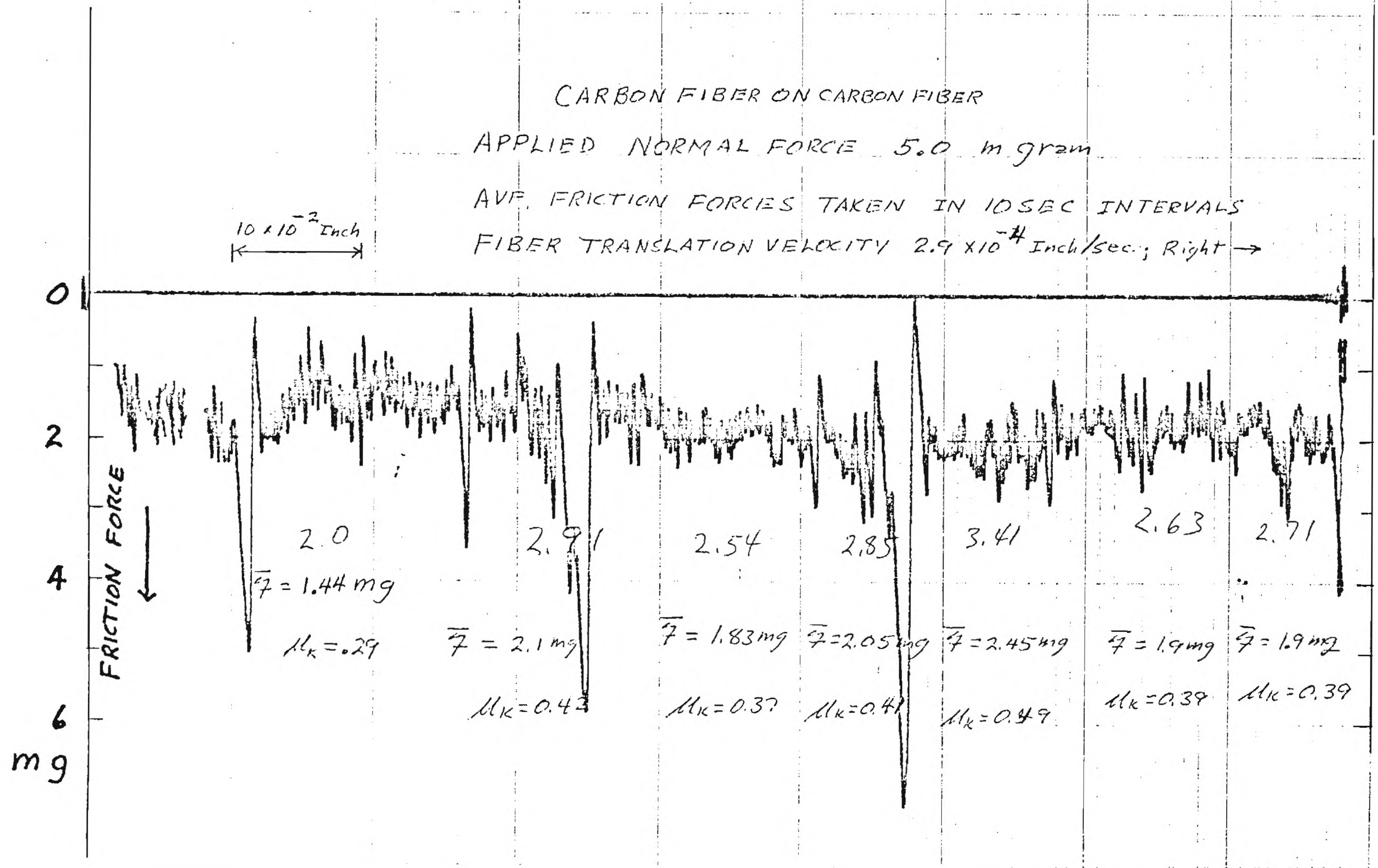
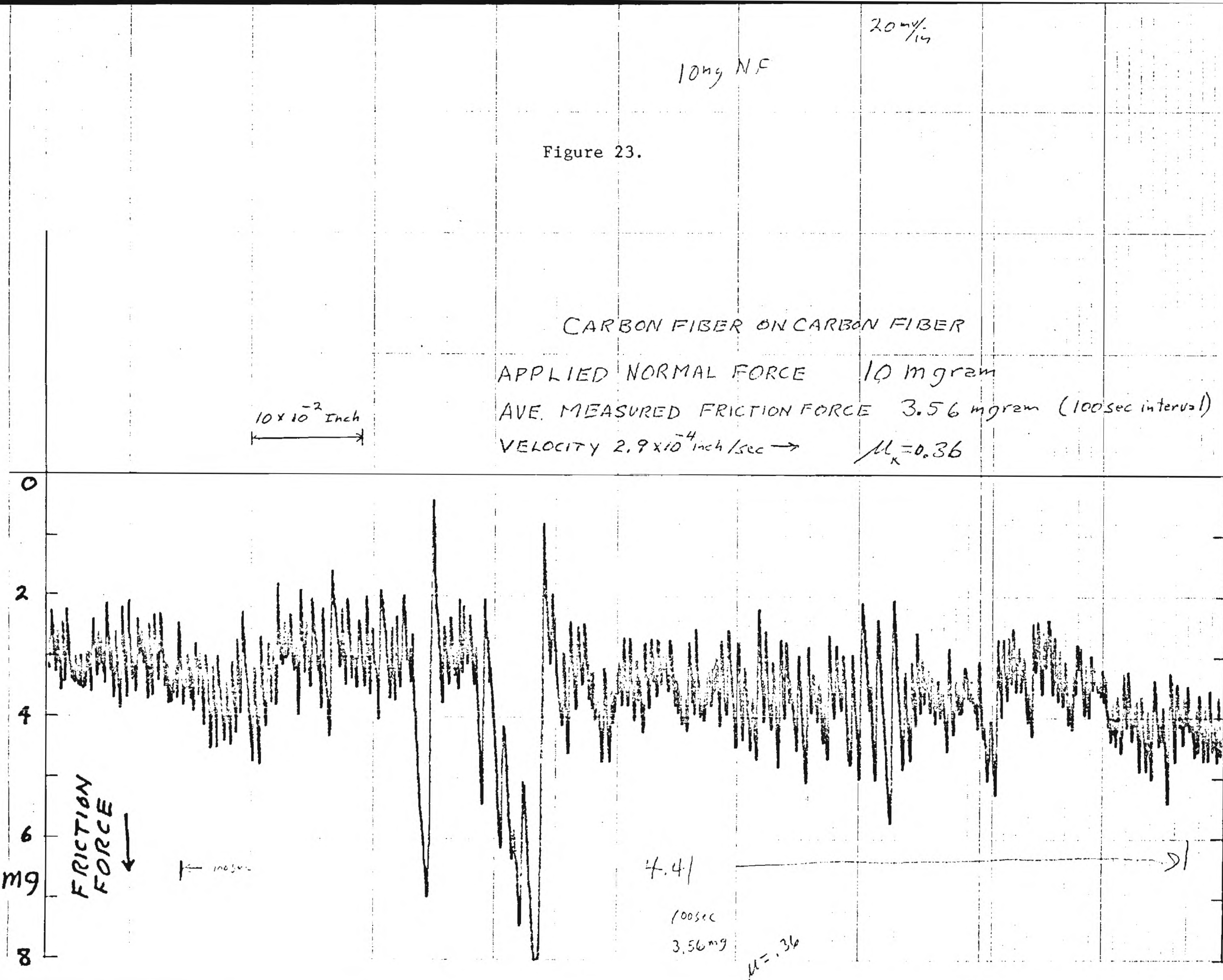


Figure 23.


20 mv/in
10 mg NF
CARBON FIBER ON CARBON FIBER
APPLIED NORMAL FORCE 10 mgram
AVE. MEASURED FRICTION FORCE 3.56 mgram (100 sec interval)
VELOCITY 2.9 x 10^-4 inch/sec →
$\mu_K = 0.36$
10 x 10^-2 Inch
0
2
4
6
8
mg
FRICTION FORCE
100 sec
4.41
100 sec
3.56 mg
$\mu = .36$

III. BUDGET SUMMARY

Period: October 12, 1976 through March 31, 1977

Time Exhausted: 5.5 Months

Time Remaining: 6.5 Months (54%)

TOTAL

Contract	$80,122
Patent Rights	3,750
Operating Budget	$76,372

	BUDGET	EXPENDED	BALANCE	% REMAINING
Personal Services	39,679.00	16,888.31	22,792.87	57%
Retirement	3,611.00	982.70	2,628.30	73%
Materials & Supplies	5,000.00	2,899.70	2,100.30	42%
Travel	1,100.00	144.03	955.97	87%
Total Direct Charges	49,390.00	20,914.74	28,475.26	58%
Overhead	26,982.00	11,484.05	15,497.95	57%
TOTAL	76,372.00	32,398.79	43,973.21	58%

PROCESSING OF PITCH–BASED, STAPLE CARBON FIBER

By
D. S. Brookstein, A. R. Colcord, L. Konopasek, and D. J. O'Neil

November 1977

GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia

FINAL REPORT: PROJECT A-1912

PROCESSING OF PITCH-BASED, STAPLE CARBON FIBER

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D. S. Brookstein, A. R. Colcord, L. Konopasek, D. J. O'Neil
Georgia Institute of Technology

November, 1977

performed for:

Union Carbide Corporation
Carbon Products Division
Cleveland, Ohio 44101

ACKNOWLEDGEMENTS

The research reported herein was performed under Project A-1912 by the Georgia Institute of Technology contracting through the Georgia Tech Research Institute. This was a collaborative effort of the Chemical and Material Sciences Division, Engineering Experiment Station and the School of Textile Engineering.

Program manager for this study was Dr. Daniel J. O'Neil, Chief, Chemical and Material Sciences Division. Dr. David S. Brookstein, Assistant Professor, School of Textile Engineering, was the Principal Investigator. Mr. Alton R. Colcord, Senior Research Engineer, Chemical and Material Sciences Division, acted as co-principal investigator. Mrs. Ludmilla Konopasek, Research Engineer, was in charge of laboratory testing and evaluation. Other members of the Chemical and Material Sciences Division who participated in this study include Ms. Rosanne Philen, Ms. Estella Sye, and Ms. Y. Patti Yi.

The assistance of the Southern Regional Research Center, U. S. Department of Agriculture, New Orleans, Louisiana--in particular, Dr. Devron Thibadeux and his staff--is gratefully acknowleged.

The cooperation of the staff of Union Carbide at the Parma Technical Center and at Greenville, S. C. is also gratefully acknowledged.

SUMMARY

This report describes the research aimed at developing materials handling systems for processing of brittle, pitch-based staple carbon fibers which are presented in the form of randomly-oriented mats. While the initial objective of the program was to demonstrate the feasibility of producing a staple carbon yarn, the primary focus became one of alignment and attenuation of the mats into preferentially-oriented, aligned webs.

Chapter I describes the process for handling, alignment, and attenuation of mat and its effect on fiber and mat properties. Chapter II describes the procedures for determination of the orientation of random and aligned mats on the basis of the mechanical properties of, (a) adhesively-bonded mats and, (b) carbon reinforced plastic composites. Chapter III summarizes the conclusions and recommendations arising from this study.

The major results follow:

(1) Materials handling operations have been developed for the brittle, carbonized fibers with little resultant deterioration of structural integrity.

(2) An alignment and attenuation process has been developed for conversion of randomly-oriented mat into preferentially-aligned webs. An invention disclosure has resulted.

(3) Composites of the random mat and aligned web with a phenoxy thermoplastic matrix and with thermosetting polyester matrices, demonstrate

the preferential alignment by improved elastic modulus values.

(4) Recommendations for fabrication of composites from random and aligned mats of discontinuous fibers were developed.

(5) The feasibility of spinning "pre-ox", pitch-based staple fibers into a yarn has been demonstrated.

The results of this study indicate that further development work is required to optimize the alignment and attenuation process with a view to the elimination of drafting waves and achievement of an aligned web of controlled thickness. Additionally, the development of composite fabrication techniques and matrix systems will be necessary to exploit the inherent superior mechanical properties of the discontinuous fibers.

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LIST OF FIGURES (cont'd)

CHAPTER 1. PROCESS INVENTION AND DEVELOPMENT

1.1 Introduction

The Carbon Products Division of the Union Carbide Corporation has in production a unique process to manufacture randomly-oriented mesophase pitch-based staple carbon fiber mat. The nature of the process is responsible for a wide distribution of fiber properties within the mat. Moreover, these fibers are exceptionally brittle and require sophisticated techniques for handling them since they are easily subject to both linear breakage and pulverization.

Ordering the fibers into aligned linear assemblies has been addressed in this chapter. A system for the alignment and attenuation of randomly oriented mat has been invented and developed. The results of the tests on the aligned and attenuated mat presented in Chapter 2 clearly indicate an increase in the structural performance of materials fabricated from this mat.

This chapter concerns the invention and development of a method for aligning and attenuating mat without major levels of fiber damage.

1.2 Concept of Alignment and Attenuation

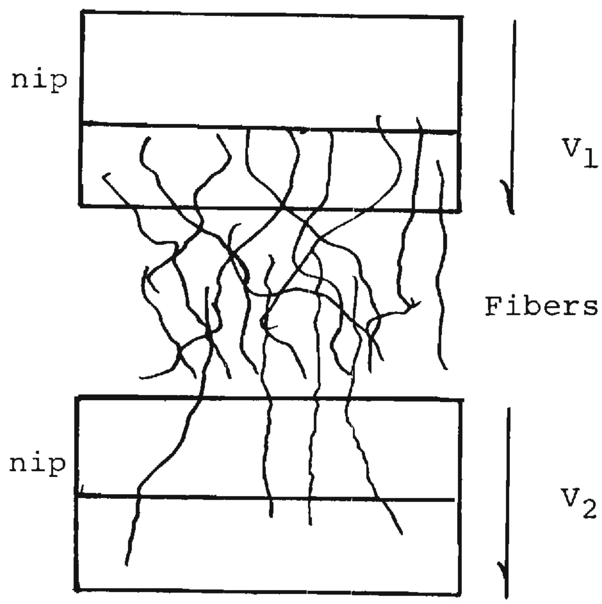
Pitch-based staple fibers are configured presently in a randomly-oriented three-dimensional mat. The fibers, whose lengths range from less than one centimeter to about eight centimeters, are brittle with breaking strains less than 1%. Accordingly, handling the fibers requires extreme care and attention to their tendency to either break or pulverize as a result of excessive handling. Moreover, any engineering scheme destined to manifest an aligned structure must do so by attenuating small groups of fibers in a fashion which will yield aligned structures. The significance of these aligned structures derives from the need to obtain either yarn or composite moduli where fiber modulus is most effectively translated.

The general system chosen for alignment and attenuation contains embodiments found commonly in the basic textile industry. The essential embodiment is that of being able to accelerate small groups of fibers by the positive drive actions of two sets of gripping surfaces.

Alignment results from accelerating the leading end of a fiber with a moving surface while the remainder of the fiber is under the influence of friction between itself and other fibers moving slower as they are under the control of the slower moving surface. This concept is depicted in Figure 1.1.

Figure 1.1

CONCEPT OF ALIGNMENT AND ATTENUATION



V_2 is greater than V_1

Attenuation or drafting is a consequence of the condition of uniform mass flow rate through the system. That is, the number of fibers multiplied by their linear speed at any station in the process must be constant. Therefore, an increase in linear speed must be accommodated by a thinning or reduction of number of fibers in the fiber flow. The condition of uniform mass flow does not always obtain.

For example, if during attenuation the distance between the two gripping surfaces is much less than the longest fibers so that many fibers are held at the same time by both back and front surface, the material refuses to draft properly. If the setting is just too close, the front surface delivers small undrafted tufts of fibers; this effect is known as spewing. Fibers are also broken when the setting is too close.

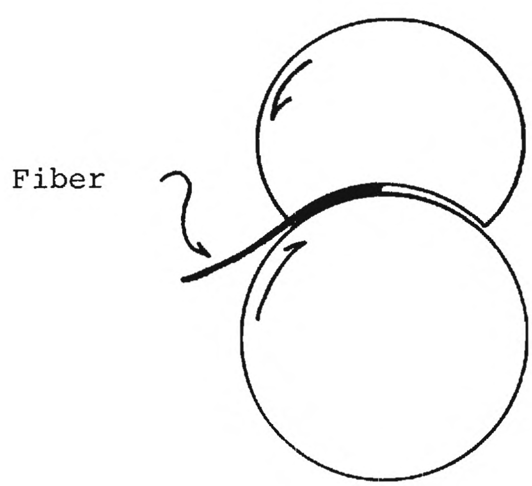
Mat contains fibers of different lengths and, when the setting is wide enough to avoid spewing, there are many fibers which are shorter in length than the surface setting. The rear ends of these fibers are released by the back surface before their front ends have reached the front surface. The lack of perfect straightness and parallelism of the fibers has a similar effect, because fibers which are curled or crimped and those which lie at an angle to the length of the sliver do not reach from the back to the surface nip.

Consider one of the shorter fibers, at the moment of its release by the back surface. It is moving at the speed of the back surface and is partly surrounded by fibers which are held by the back surface and which by friction against it, it tends to keep moving at the back surface speed. It is, however, not gripped by either surface, and is not therefore controlled directly by them, but is carried forward solely by the other fibers. Such a fiber is called a floating fiber.

If, because of the friction between them and the fibers which are still held by the back surface, all the floating fibers continue to move at back surface speed until the front ends reach the front surface nip then we have perfect attenuation.

The floating fibers are, however, also in contact with other fibers which are held by the front surface, and therefore tend to be dragged forward at front surface speed. For some of the floating fibers the drag exerted by the fast-moving fibers exceeds that of the slow-moving fibers, and they are pulled forward at front surface speed, and reach the front surface earlier than they should. This means that the number of fibers held by the front surface becomes greater than it would otherwise have been, so that a thick place is formed under the front surface. There are now more fibers moving at front surface speed to drag forward the floating fibers, and so the dragging forward tends to continue. It does not continue indefinitely, because the removal of floating fibers from the drafting zone causes the mat in this region to be thinner than normal. This thin place moves up to the front surface, causing a reduction in the number of fast-moving fibers, and a consequent reduction in the number of floating fibers being dragged forward; the whole process then repeats. In this way the motion of the floating fibers causes a succession of alternate thick and thin places in the drafted material. The short fibers tend in fact to emerge from the front surface in clumps. This succession of thick and thin places is called a drafting wave.

The primary objective of this project was to design a process to align and attenuate either pre-oxidized or carbonized pitch staple fibers from randomly oriented mat. Since these mat fibers are extremely brittle they cannot be subjected to severe treatment. Accordingly, the fibers cannot be gripped too harshly at the processing surface nor can they be subjected to severe deformation. With these constraints considered, a novel approach was employed to affect attenuation and alignment. The essence of this approach consisted of gripping the fiber over a relatively long length of the fiber rather than subjecting the fiber to a high transverse load at one end. This concept is illustrated below.



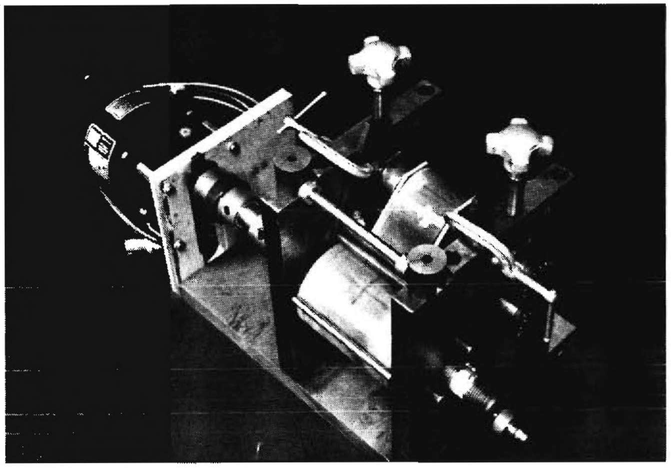
1.3 Device to Align and Attenuate

Attenuation is a consequence of mass continuity throughout the fiber handling system. That is at any station in the fiber flow the mass flow rate must be equal to the mass flow rate at any other station. Accordingly, at all stations the product of the number of fibers and their linear velocity must be constant. Consequently, whenever there is acceleration of fiber flow a reduction in the fiber flux must be present. This reduction in flux is identified as attenuation.

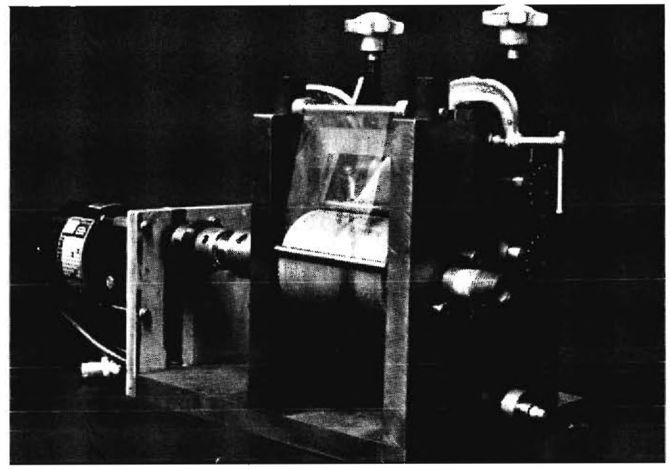
The system designed for alignment and attenuation is illustrated in Figure 1.2. A set of engineering drawings of this system is provided in Appendix A. The means of operation of the device are as follows (Refer to Figure 1.3). Unaligned mat is fed into the system at position 9. The mat is gripped immediately by a set of soft spongy rollers. The use of soft spongy rollers allows a significant level of compressive force to be applied transverse to the fiber axis without causing fiber damage. That is the transverse pressure on the fiber is limited by the ability of the soft feed rollers to deform. Correspondingly, the compressive forces on the fibers at feeding are widely distributed. The radius of the rollers is 1.0 inches. The sponge rubber thickness is .50 inches. After the mat exits the delivery rollers, auxillary transverse pressure remains on the fibrous assembly due to the action of the aprons (7). Aprons are employed commonly to carry small fiber fluxes to the next processing station. The transverse pressure minimizes the opportunity

Figure 1.2

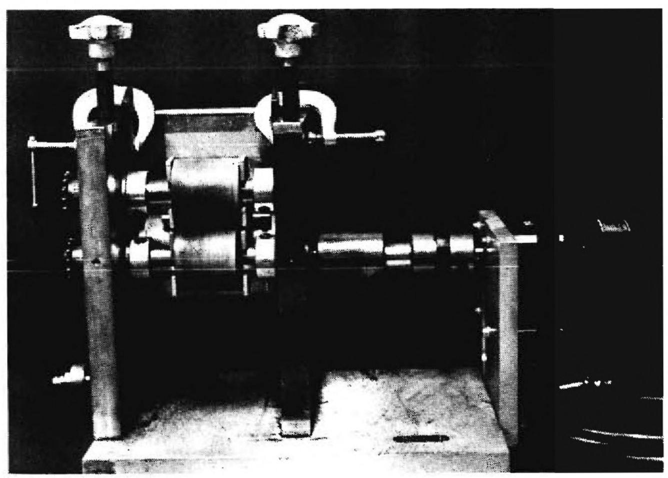
ALIGNMENT AND ATTENUATION DEVICE



TOP VIEW



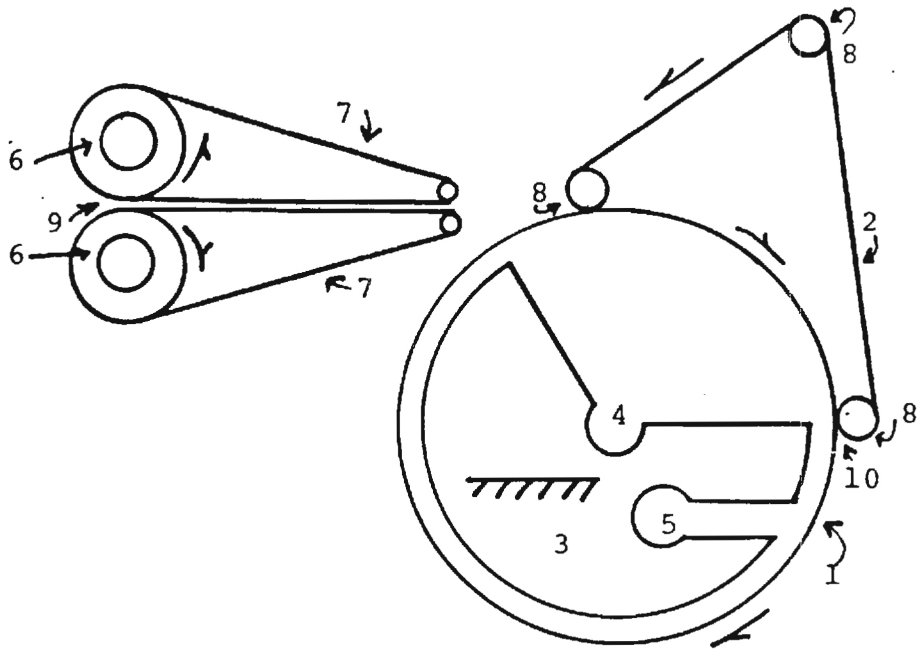
SIDE VIEW



BACK VIEW

Figure 1.3

DEVICE TO ALIGN AND ATTENUATE STAPLE PITCH-BASED CARBON FIBERS



1. Sintered metal porous roller-rotates
2. Flexible air impermeable belt
3. Fixed inner bearing with pressure and vacuum slots-fixed
4. Vacuum slot
5. Pressure slot
6. Spongy rollers
7. Apron
8. Idlers
9. Mat entrance
10. Mat exit

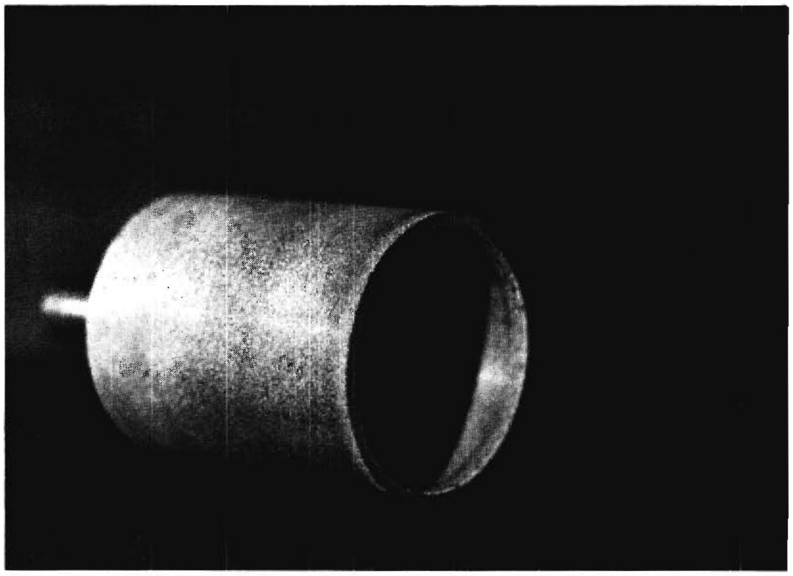
for drafting wave formation. This phenomena of drafting wave formation was discussed in Section 1.2. The fibers moving at the speed of the feed rollers now traverse to the surface of the vacuum roller (1).

This roller was fabricated from porous Type 316 Stainless Steel seamless tubing provided by the Mott Metallurgical Corporation. The filtration rating of the tube is 20 microns. The dimensions of the roller are 4.0" O.D., 0.125" thickness, 3.75" width. This roller was driven directly by a variable speed motor. A photograph of this roller is given in Figure 1.4. A stationary Teflon bushing is inserted inside the roller (Figure 1.4). The diameter of this roller is 3.73". Accordingly, there is a 2 mil difference between the Teflon diameter and the roller diameter. The Teflon bushing has a 120° pie shaped section (4) cut from its surface. This space is vented to a high capacity vacuum blower capable of drawing 92 inches of water and 400 SCFM against atmospheric pressure.

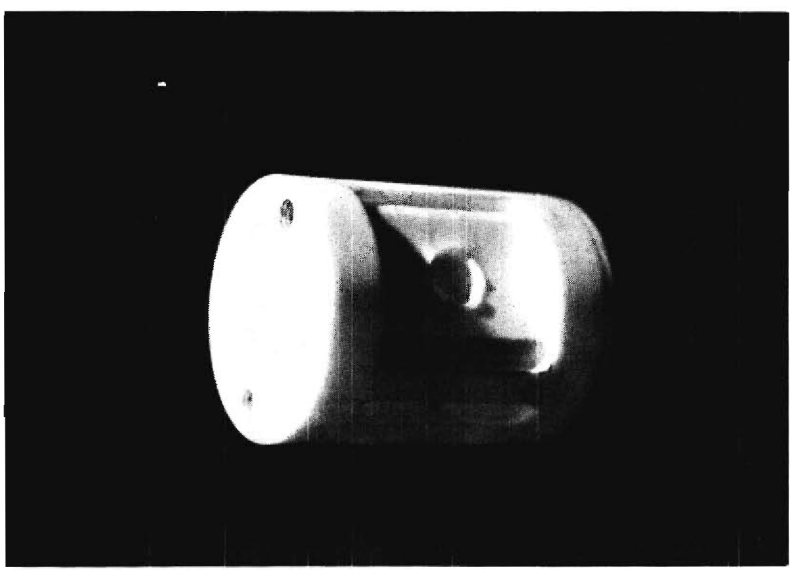
An impermeable polyurethane film belt (2) rides along the vacuum roller surface. The belt is driven by the frictional forces between the belt and roller. These forces are derived from the normal forces created by the differential pressure across the belt. These normal forces also provide the nipping action which grabs the leading edge of the fiber and accelerates it forward providing alignment and attenuation.

Figure 1.4

VACUUM ROLLER ASSEMBLY



POROUS VACUUM ROLLER



TEFLON BUSHING

This nipping is extremely advantageous with regard to limiting fiber crushing for the mat fibers are exposed to minimal transverse compressive forces at any one point on the fiber. For example, if the vacuum blower draws 60.00" of water, the pressure on the fiber is only about 3 psi. The fibers withstand this pressure with little difficulty and without subsequent crushing.

As the aligned mat exits, it is doffed from the vacuum roller by a jet of air blown through a small slot (5). The line pressure of the air before this slot is 30 psi.

Photographs of the mat before and after processing are shown in Figure 1.5.

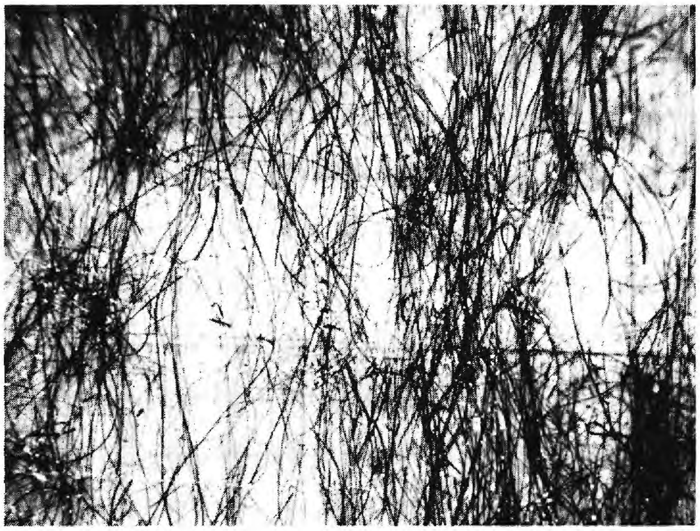
1.4 Fiber Properties Before and After Alignment and Attenuation

Mat carbon fibers are inherently brittle. Moreover some of the fibers are manufactured inadvertently with permanent kinks and bends. Of course, this condition indicates an opportunity for the fibers to break when they are straightened during alignment and attenuation. The strength of both yarns and fiber reinforced composite materials depends somewhat on fiber length; long fibers have a greater surface area than short fibers to transfer inter-fiber shear stresses. Accordingly, fiber length before and after processing must be determined. In addition to fiber length, fiber strength must be examined to determine the translation of fiber strength to overall composite strength.

Figure 1.5

PRE-OXIDIZED MAT AND WEB

UNALIGNED PRE-OZIDIZED MAT
MAG. 8.5 X



ALIGNED PRE-OXIDIZED WEB
MAG. 8.5 X

At the onset of this project, both Union Carbide and Georgia Tech personnel decided that the most promising method for processing mat fiber would involve the use of pre-oxidized pitch fiber since this fiber has a relatively high extension to break or, "handability". Accordingly, a series of length determinations were carried out with fibers heat treated at different conditions. Then, following alignment and attenuation, the mat was reexamined and the new fiber length distributions were determined. From these length distributions, one can determine the effect of fiber processing on fiber length.

Fiber sampling was accomplished by withdrawing fiber from the mat with a pencil point covered with double sticky tape. Accordingly, the fibers were not usually broken as they were removed and positioned against a scale for length determination.

The dimensional properties of pre-oxidized pitch fibers manufactured in Greenville in November 1976 for this project are listed in Table 1.1. Correspondingly, the physical properties of these same fibers are listed in Table 1.2. For both tables, the type of fiber listing refers to proprietory processing conditions determined by Union Carbide. A perusal of the data indicates that Type 6 would be the fiber which would yield the most promising set of results with the attenuation and alignment device. Type 6 fiber has a high average modulus 1.2×10^6 psi (8.28 Gpa) a moderate average breaking extension of 3.2% and an average length of 4.54 cm. However, the %

Table 1.1

Dimensional Properties of Pre-Oxidized Pitch Fibers

No.	Type	Diameter, μ			Length, cm			Aspect Ratio
		Mean, μ	SD, μ	% C.V.	Mean, cm	SD, cm	cm %	
1	132	10.5	4.0	38.5	3.79	1.71	45.2	3609
2	133				3.14	1.66	52.7	2990
3	131				4.38	1.93	44.1	4171
4	120				2.54	1.18	46.6	2419
5	322	7.7	4.4	57.9	4.10	1.80	44.0	5324
6	323				4.69	1.89	40.2	6091
7	330				2.72	1.25	46.4	3532
8	321				4.69	2.04	43.6	6091
9	423	7.0	3.2	45.52	3.05	1.38	45.1	4357
10	422				3.95	1.78	45.1	5643
11	430				2.46	0.94	38.4	3514
12	421				3.66	1.79	49.0	5229
13	522	14.4	5.4	37.8	4.09	1.99	48.6	2840
14	530				2.71	1.17	43.1	1882
15	521				4.34	1.82	42.0	3014
16	6	11.7	4.6	39.1	4.54	2.04	45.0	3880

TABLE 1.2 PRE-OXIDIZED FIBER PHYSICAL PROPERTIES

No.	Type	Diameter μm	Density g/cm^3	Linear density den(tex)	Breaking load, pounds (gf)			Specific strength, psi (Tenacity gf/den)			Breaking extension, %			Young modulus, psi (Tensile modulus, g/den)
					Mean value, pounds(gf)	Standard deviation, pounds(gf)	Variation Coefficient %	Mean value, psi(gf/den)	Standard deviation, psi(gf/den)	Variation Coefficient %	Mean Value %	Standard deviation, %	Variation Coefficient %	
1	132	10.5	1.35	1.05(0.11)	$6.2X10^{-3}$ (2.82)	$2.8X10^{-3}$(1.26)	44.8	46321 (2.68)	20752 (1.20)	44.8	7.56	2.78	36.9	$0.6X10^{6}$(3.54)
2	133				$6.3X10^{-3}$ (2.86)	$2.3X10^{-3}$(1.04)	36.4	46978 (2.71)	17100 (0.99)	36.4	2.83	0.79	28.6	$1.7X10^{6}$(95.8)
3	131				$5.6X10^{-3}$ (2.56)	$2.2X10^{-3}$(1.00)	38.9	42050 (2.43)	16357 (0.95)	38.9	4.67	2.47	52.9	$0.9X10^{6}$(51.9)
4	120				Breaking load showed to be less than 0.5g									
5	322	7.7	1.35	0.57(0.06)	$7.3X10^{-3}$ (3.31)	$1.7X10^{-3}$(0.79)	23.9	101100(5.85)	24163 (1.39)	23.9	2.94	0.79	26.9	$3.4X10^{6}$(198.8)
6	323				$6.0X10^{-3}$ (2.71)	$2.1X10^{-3}$(0.97)	35.9	82774 (4.78)	29715 (1.72)	35.9	3.0	0.68	23.0	$2.8X10^{6}$(161.9)
7	330				Breaking load showed to be less than 0.5g									
8	321				$6.2X10^{-3}$(2.82)	$2.0X10^{-3}$(0.93)	33.0	86133 (4.97)	28424 (1.64)	33.0	2.78	0.68	24.1	$3.1X10^{6}$(178.9)
9	423	7.0	1.35	0.47(0.05)	3 $X10^{-3}$(1.35)	$2.0X10^{-3}$(0.89)	65.7	49893 (2.89)	32780	65.7	2.15	0.89	41.5	$2.3X10^{6}$(133.9)
10	422				$5.2X10^{-3}$(2.36)	$2.6X10^{-3}$(1.16)	49.2	87036 (5.03)	42822 (2.47)	49.2	2.98	0.94	31.0	$2.9X10^{6}$(168.7)
11	430				Breaking load showed to be less than 0.5g									
12	421				$5.0X10^{-3}$(2.27)	$1.7X10^{-3}$(0.79)	35.0	83821 (4.84)	29337 (1.69)	35.0	3.39	0.84	24.3	$2.5X10^{6}$(143.1)
13	522	14.4	1.35	1.98(0.02)	$7.0X10^{-3}$(3.18)	$3.4X10^{-3}$(1.53)	47.9	27772 (1.60)	13303 (0.83)	47.9	2.83	0.68	24.8	$1.0X10^{6}$(56.7)
14	530				Breaking load showed to be less than 0.5g									
15	521				$6.5X10^{-3}$(2.97)	$2.6X10^{-3}$(1.18)	39.6	25938 (1.49)	10271 (0.59)	39.6	2.99	0.63	21.7	$0.9X10^{6}$(50.2)
16	6	11.7	1.35	1.31(0.14)	$6.3X10^{-3}$(2.87)	$2.7X10^{-3}$(1.21)	42.31	37968 (2.19)	16060 (0.93)	42.3	3.2	1.21	37.92	$1.2X10^{6}$(68.5)

coefficient of variation for all of these properties is on the order of 40%, indicating significant fiber to fiber non-uniformity.

The inherent non-uniformity of the fibers produced at the Greenville plant is illustrated best by the series of scanning electron micrographs presented in Figure 1.6.

A case of severe fiber disfiguration is illustrated in Figure 1.7. Here a deep gouge which will probably render the fiber useless with regard to tensile properties is seen.

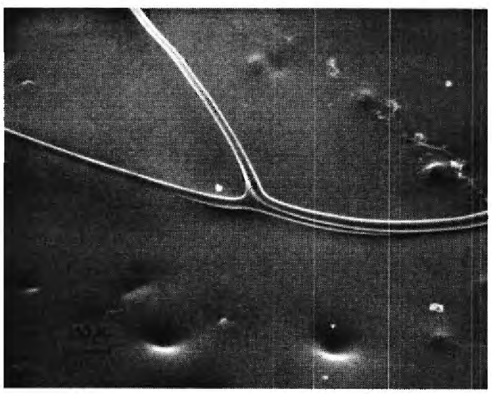
Mat produced in Greenville has a width of 18 inches; the prototype alignment and attenuation device works with a mat width of about 1". Accordingly, the mat must be cut narrower before processing. This cutting reduces the length of some of the fibers which are at an angle to the fiber manufacturing or process flow axis. Therefore, for all comparisons of the effect of fiber processing on fiber length, we will use the fiber length distribution in the mat after cutting as the baseline data.

This distribution possesses a slight skew to the shorter, fiber lengths with the average fiber length being 3.56 cm. However, the % coefficient of variation is 50.8% indicating a significant variation in fiber lengths. Discussions with personnel at the Greenville plant indicated that this length variation is normal for most processing conditions employing the old blow spinning device located at Greenville prior to July 1977.

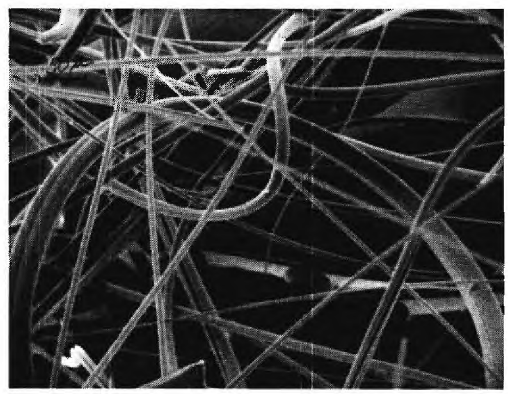
Figure 1.6

NONUNIFORMITY OF SURFACE STRUCTURES, SHAPE AND DIAMETER
IN PITCH FIBERS

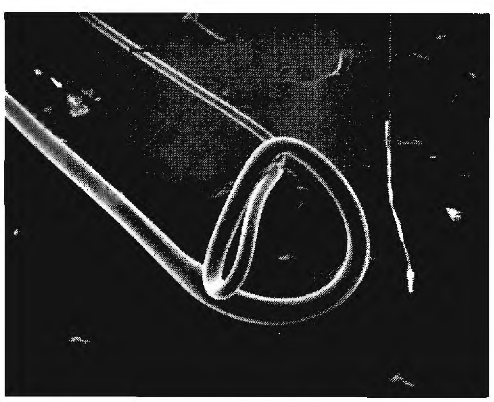
1) HOLES AT THE SURFACE 2)

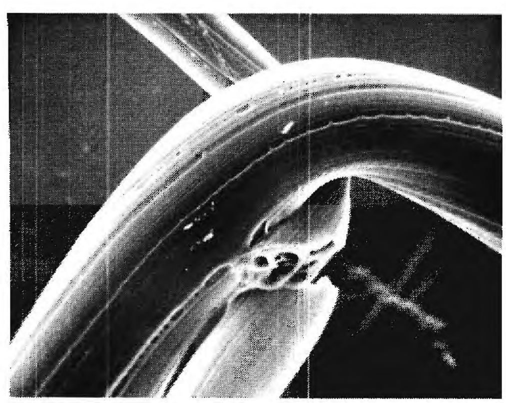


3) "BRANCHING"



4) VARIATIONS IN DIAMETER





5) TAPERING SHAPE OF FIBER AND HOLES AT THE SURFACE AND INSIDE THE FIBER 6)

Figure 1.7

DEEP CREVICE ALONG THE FIBER AXIS

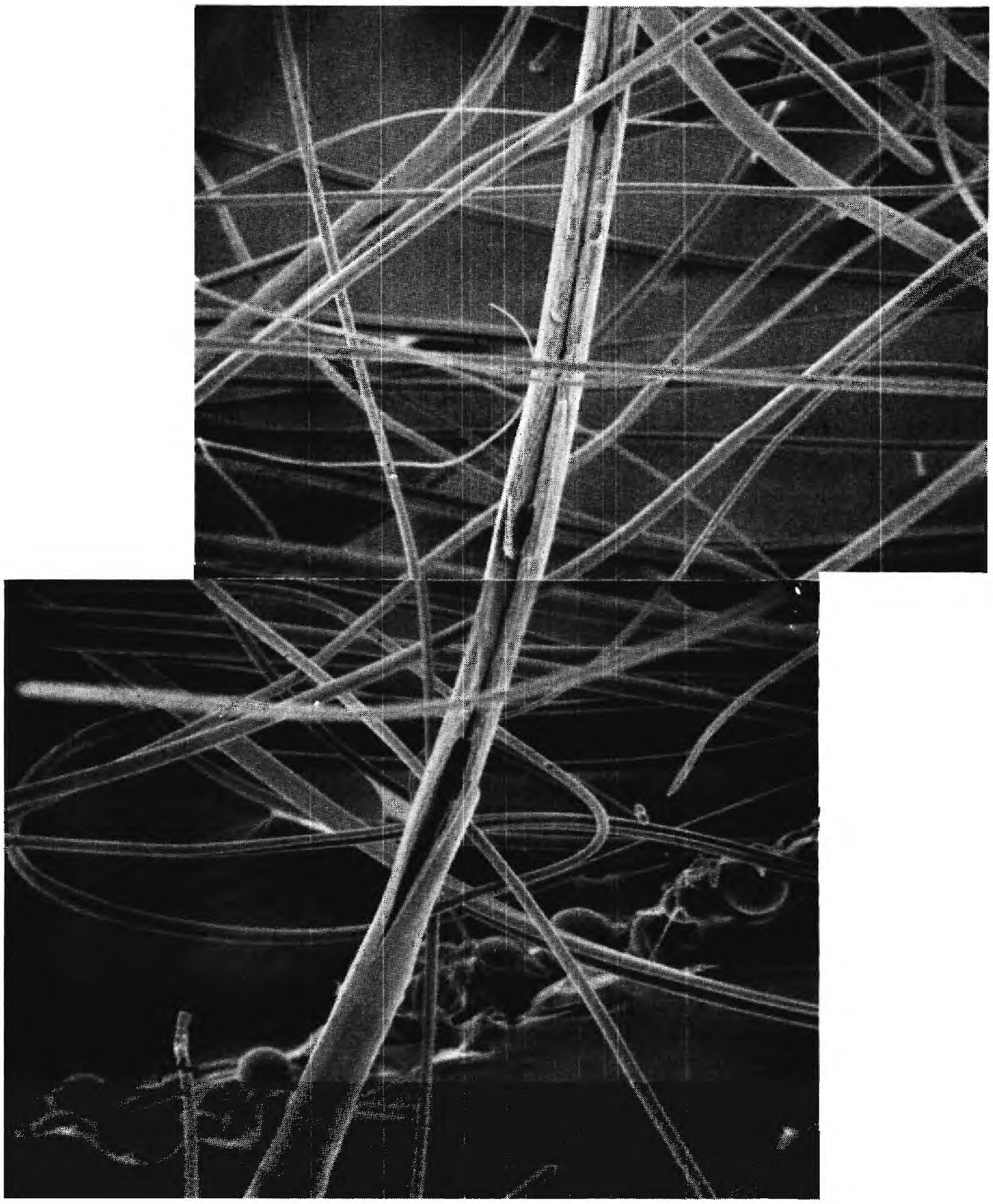
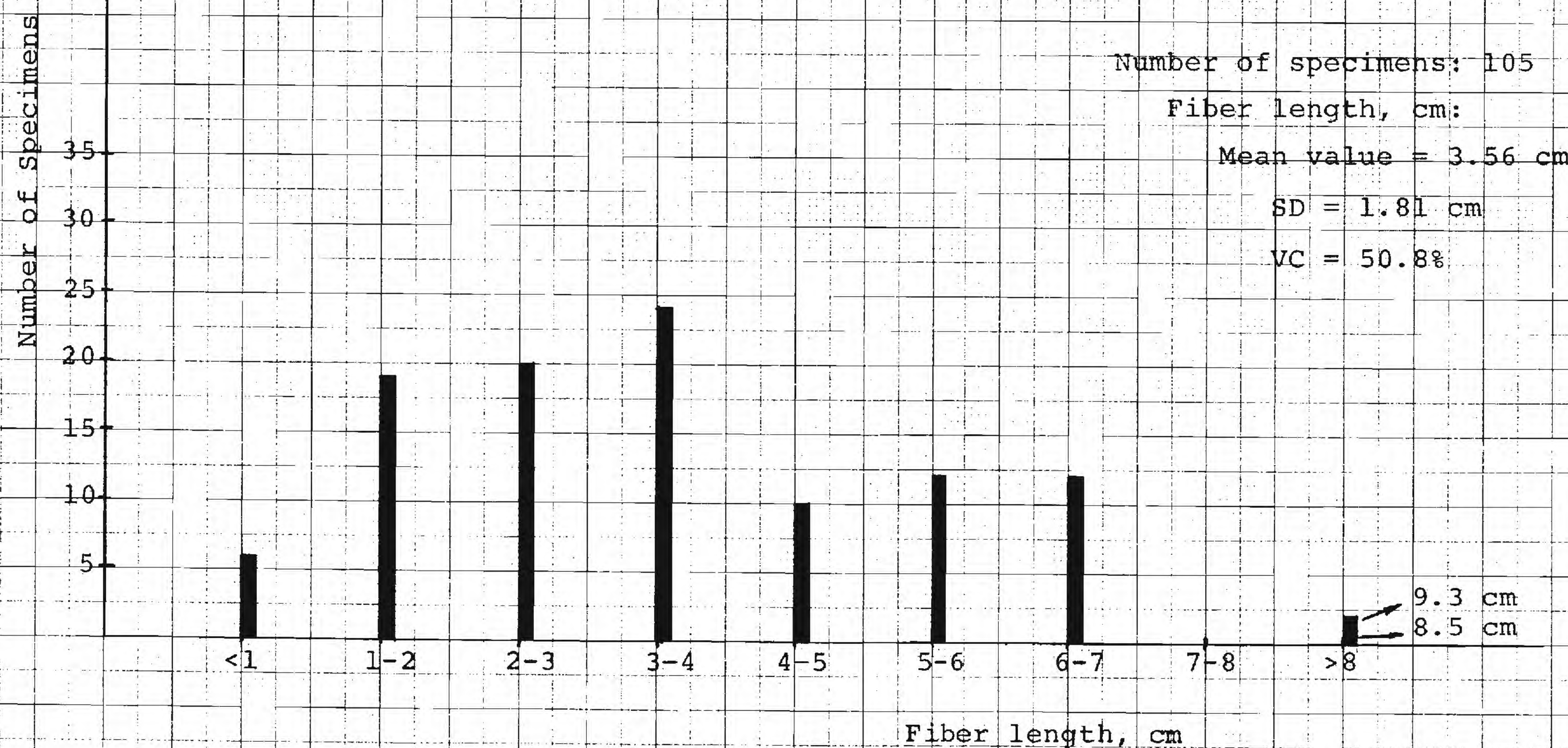


Figure 1.8

Type 6

Fiber length distribution in the mat (after it was cut) before processing



Personnel at Greenville determined the average fiber diameter and diameter coefficient of variation for Type 6 fiber. These values are 11.7 μm and 39.1% indicating an average aspect ratio of 3043. The 11.7 μm fiber diameter indicates a fiber denier of 1.34; a thin fiber by most textile standards.

Following initial characterization of Type 6 cut mat, the resulting fiber length distribution was determined after processing the mat through the device. A series of processing parameters was investigated in which both the attenuation ratio and overall speed was varied. Figure 1.9 presents the length distribution after processing with an attenuation ratio of 5.00 and a delivery speed of 1.05 cm/sec. The mean length of the fibers decreases from 3.56 cm to 2.90 cm. Moreover, it appears that the shorter fiber length is a result of rupturing fibers greater than 5.00 cm. In other words, fiber breakage is probably a consequence of having the nip of the attenuator or vacuum roller too close to the feed roller. This can be remedied but only at the expense of mat non-uniformity or drafting waves.

To check the reproducibility of the measurement technique and process, a second experiment was conducted in which the processing parameters were kept the same as above. These replication results are presented in Figure 1.10 and comparison with Figure 1.9 indicates a high level of reproducibility.

The fiber length distribution results for a range of processing parameters are provided in Appendix B. A summary of the mean fiber lengths is illustrated in Figure 1.11. Examination of this data indicates that for all processing parameters

Figure 1.9

Type 6

Test N 1

Fiber length distribution in the web, after processing the mat through the nip-rollers (1) and the vacuum roller (2)

	Speed control setting	Surface speed, cm/sec
Nip-rollers (1)	30	0.21
Vacuum-roller (2)	28	1.05

Ratio 5

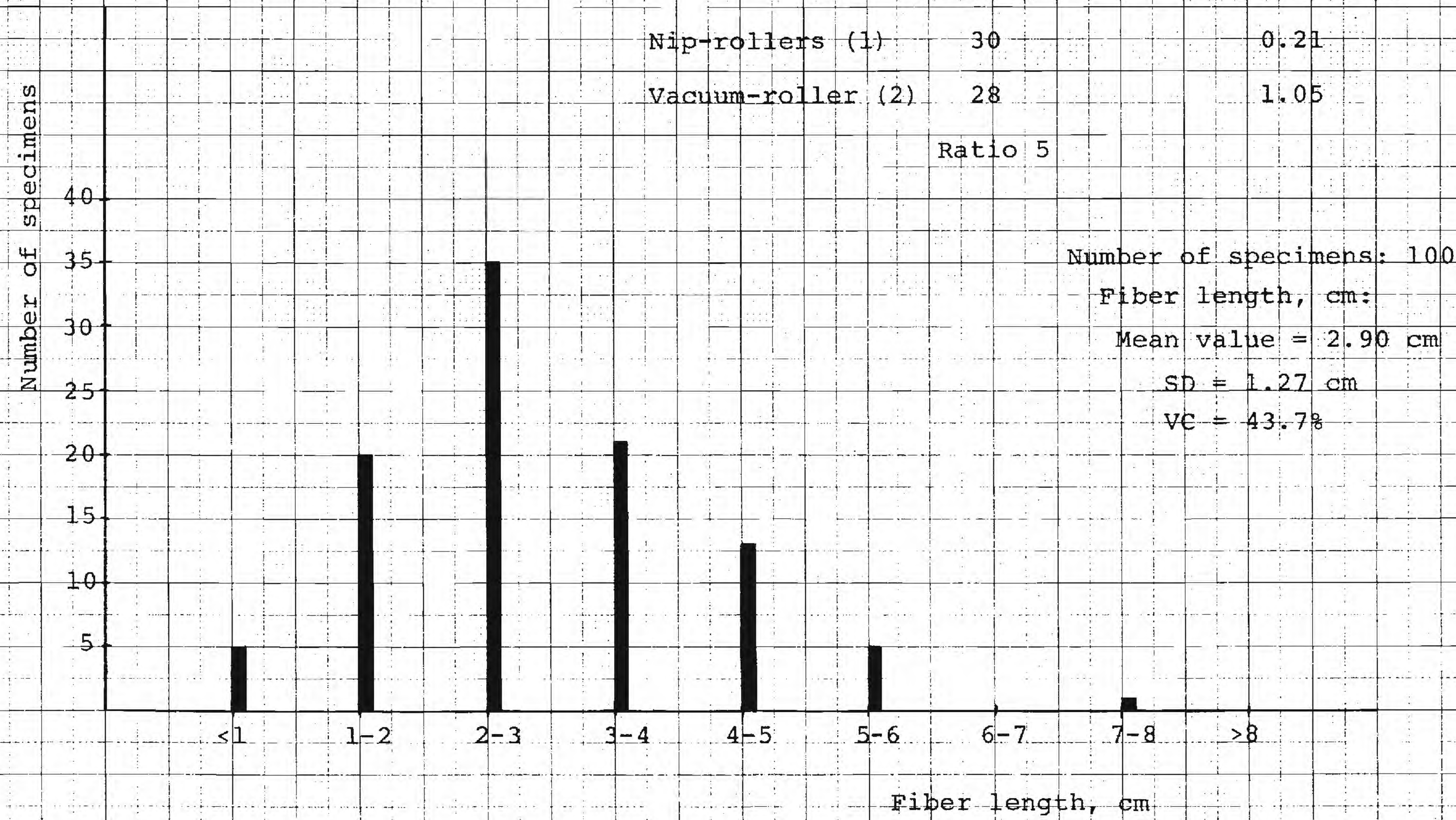


Figure 1.10

Type 6

Test No. 2

Fiber length distribution in the web, after processing the mat through the nip-rollers (1) and the vacuum roller (2)

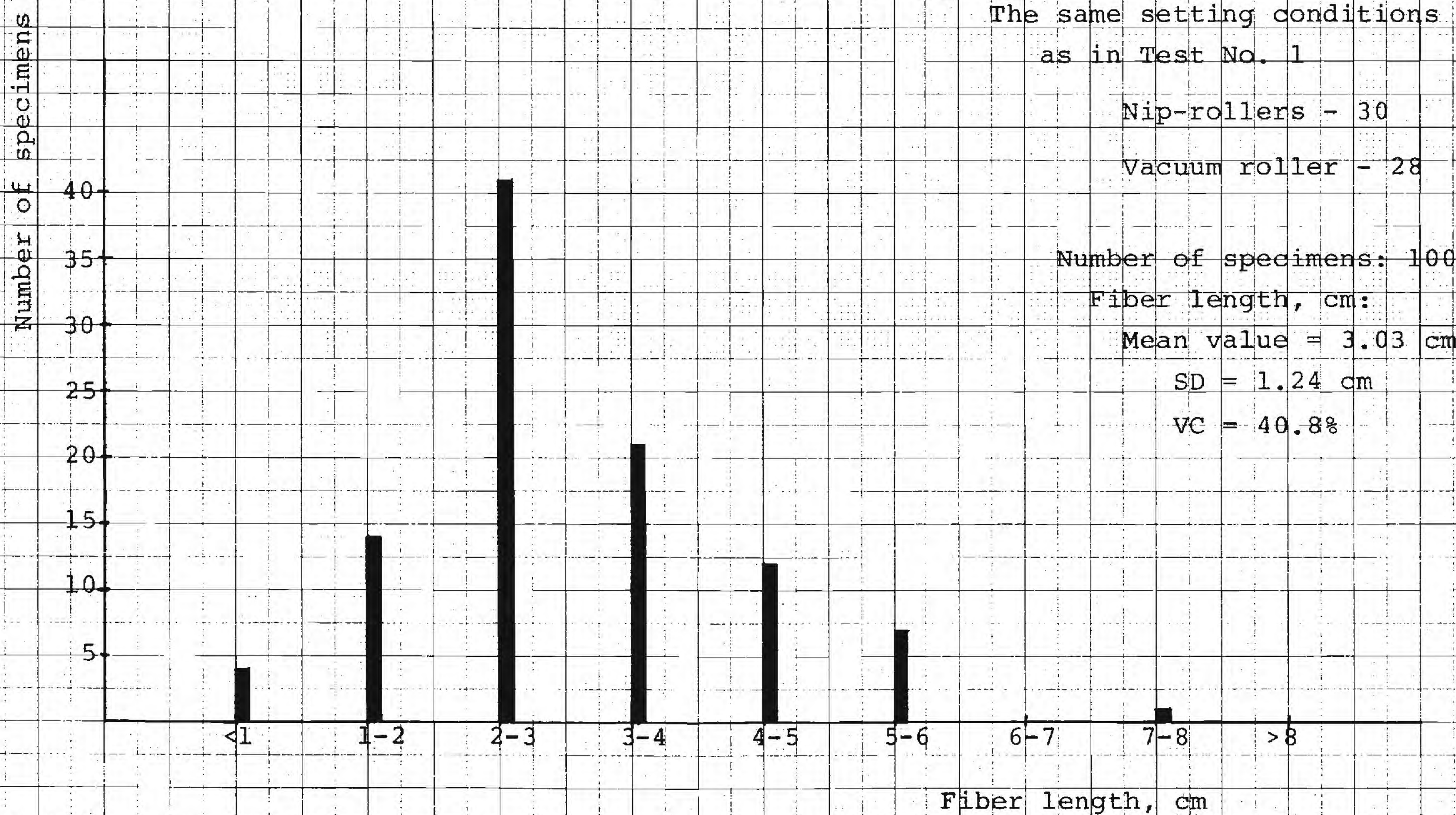
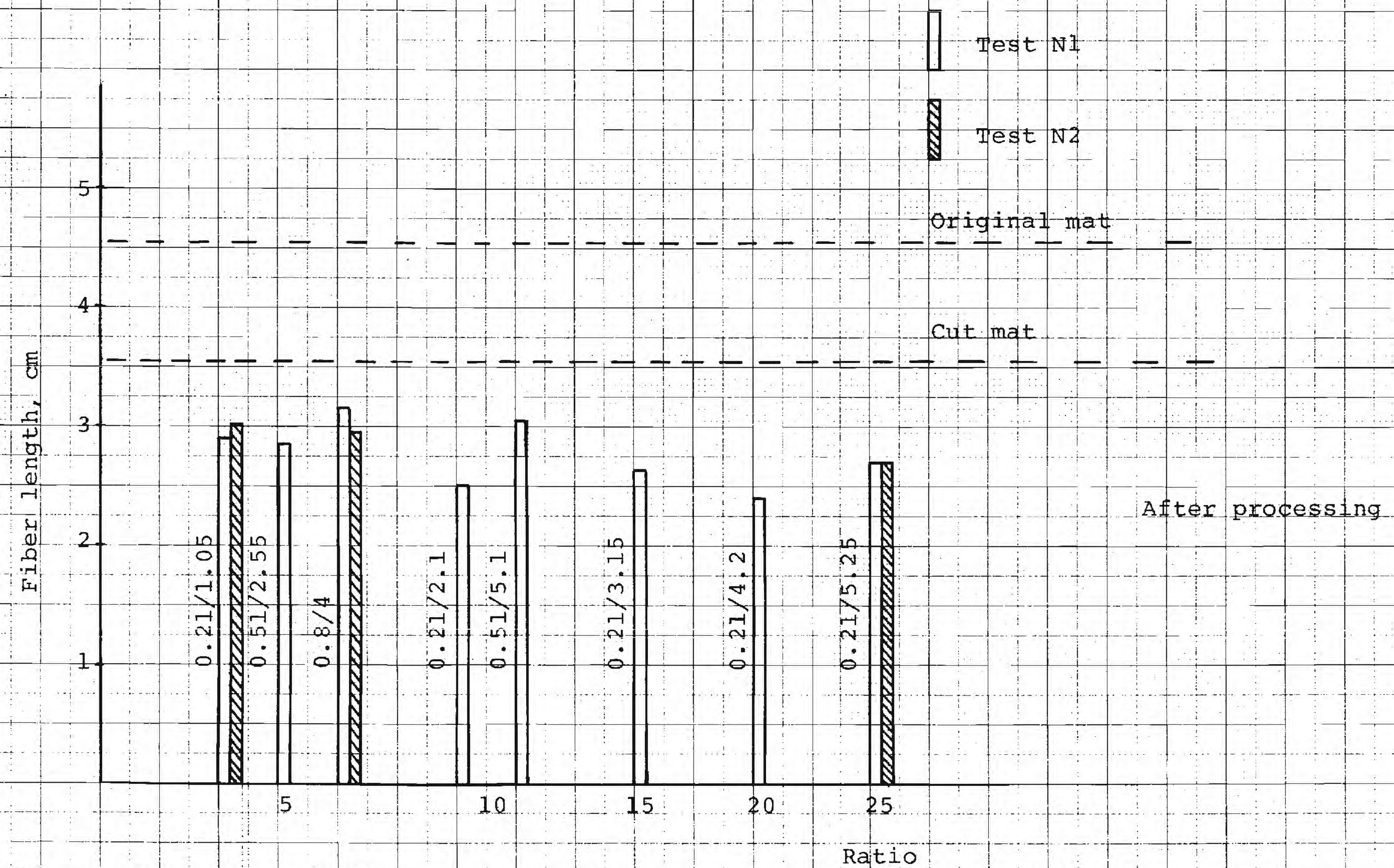


Figure I.11

Effect of processing on fiber length



the maximum fiber length deterioration is only about 30%. Hence it can be concluded that the developed system for alignment and attenuation does not affect severely the fiber length during processing.

Factors influencing the behavior of fibers in an alignment and attenuation system can be determined from a consideration of the forces involved during machine-material interaction. The restraining forces on fibers in the incoming mat must be overcome by the attenuator (i.e. vacuum roller) in order to withdraw a fiber from the mat. If the restraining forces are excessive, the impact energy of the attenuator can result in either fiber breakage or cutting. Accordingly, the ease of removal of fibers from a mat array is a function of the pressure holding the fibers together, fiber-to-fiber friction, fiber-to-fiber contact area and the degree of fiber entanglement in the mat. The pressure acting on the fibers within the mat is a function of the mechanical pressure applied by the feed rollers, the dimensions of the mat, and the geometry of opening between the feedrollers and attenuator. The pressure can be set within certain limits. The physical size of the mat can be expressed in terms of denier (linear density) and fiber density. The last factor, the geometry of the opening can also be set. The contact area between fibers is a function of the number of fibers in the mat and the surface area per fiber. Lastly, the number of fibers in the mat can be expressed as the ratio of mat denier to fiber denier and the surface area per fiber is simply proportional to the product of fiber length and square root of fiber denier. Accordingly, the restraining forces acting on fibers in the mat feed to the attenuator may be formulated as follows:

$$F_R \ \alpha \ \frac{(K)\ (\mu_f)\ (P)\ (G)\ (\text{Mat Denier})\ (\text{Fiber Length})}{(\text{dpf})^{\frac{1}{2}}\ (\text{feed rate})} \qquad (1.1)$$

P = pressure applied to feedrollers.

μ_f = coefficient of fiber to fiber friction.

G = geometry of system.

K = degree of entanglement in mat.

The force transferred to a fiber by the attenuator involves the velocity of impact, geometry of attenuator, fiber to attenuator friction, attenuator pressure and free unclamped length of fiber. The free length of fiber determined the tendency for a fiber to grip the attenuator. These variables may be expressed in the following manner:

$$F_A \ \alpha \ K(\mu_{fm})(\text{Free Length})(\text{RPM})(\text{Pressure at attenuator}) \qquad (1.2)$$

For ideal attenuation

$$F_A \ > \ F_R \qquad (1.3)$$

or

$$\frac{(\text{feed rate})(\mu_{fm})(\text{Free Length})(\text{RPM of Attenuator})(\text{Pressure at Attenuator})(\text{dpf}^{\frac{1}{2}})}{(\mu_f)\ (P)\ (G)\ (\text{Mat Denier})^2\ (\text{Fiber Length})} > 1 \qquad (1.4)$$

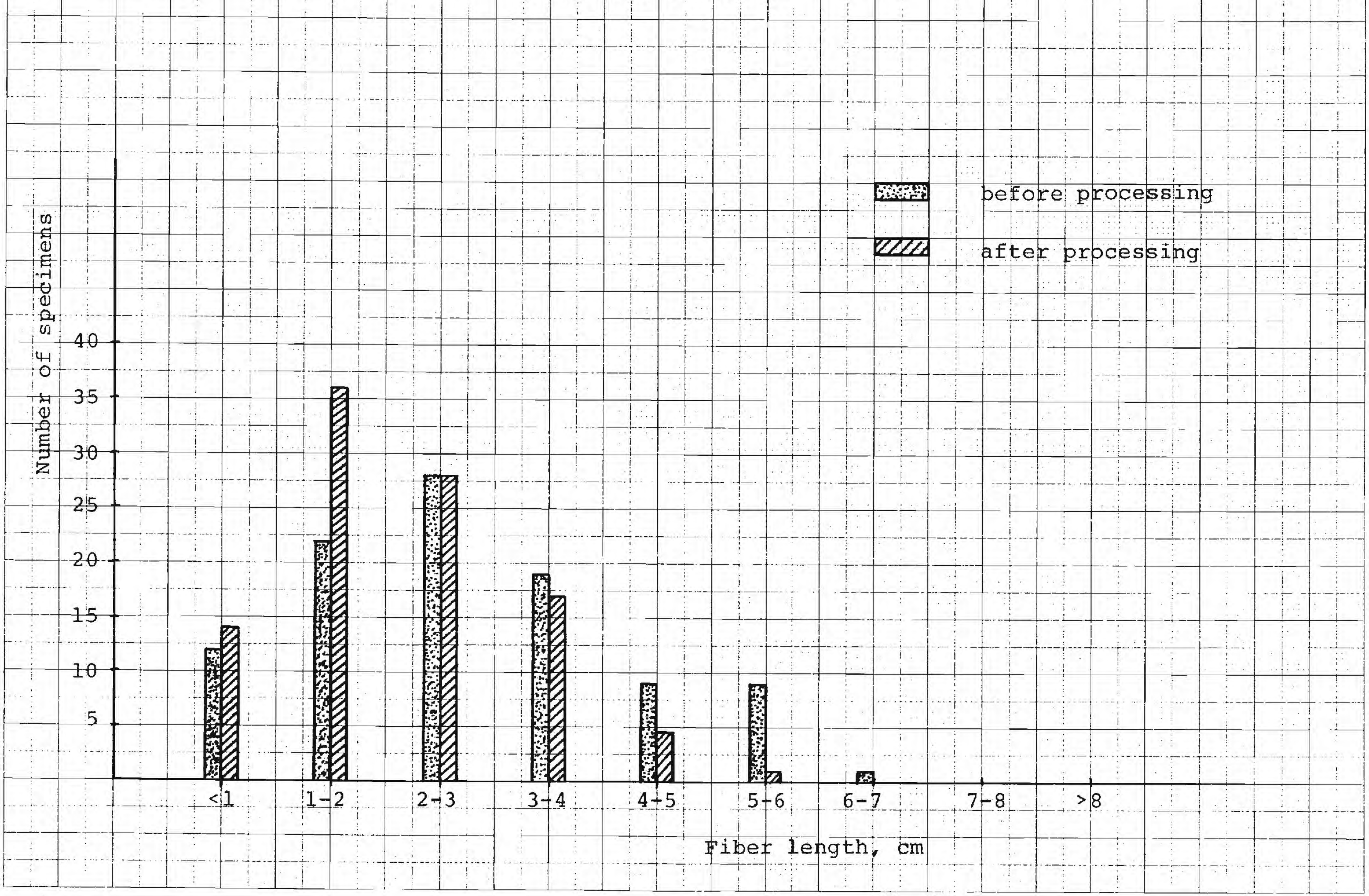
Thus the parameters for ideal attenuation would include a high fiber-to-attenuator coefficient of friction, a high attenuator pressure, a thick fiber, a moderately low feed roll pressure, a thin mat and a short fiber. The nature of the mat manufacturing system prior to July 1977 precluded the possibility of large denier fibers with moderately short lengths. Characterization of fiber dimensions indicated a relatively constant length/diameter ratio for mat fibers. It is suggested though that future mat processing developments include the possibility of manufacturing low L/D fibers to better affect attenuation.

At first the only fibers which were processed through the alignment and attenuation device were pre-oxidized fibers which were not carbonized. This choice was based on the fact that pre-oxidized fibers were considered to be more easily handled or having higher strains to break than carbonized fibers. However, during a latter segment of the project, carbonized fibers were processed through the attenuation device. These fibers were processed with moderate fiber breakage as is indicated by Figure 1.12. Accordingly, it was decided that all future work would be completed with carbonized fibers for feed material. The economic advantage of this procedure is clearly demonstrated by the fact that aligned carbonized fibers can be made continuously while pre-oxidized fibers subject to alignment and attenuation prior to carbonization would require more expensive batch processing.

1.5 Staple Yarn Manufacturing

Yarns are derived from groups of linear fiber assemblies

Figure 1.12
Carbonized fibers



which are usually twisted into a coherent structure. The purpose of twist is to provide the normal forces between fibers necessary for inter-fiber friction and to give the yarn strength.

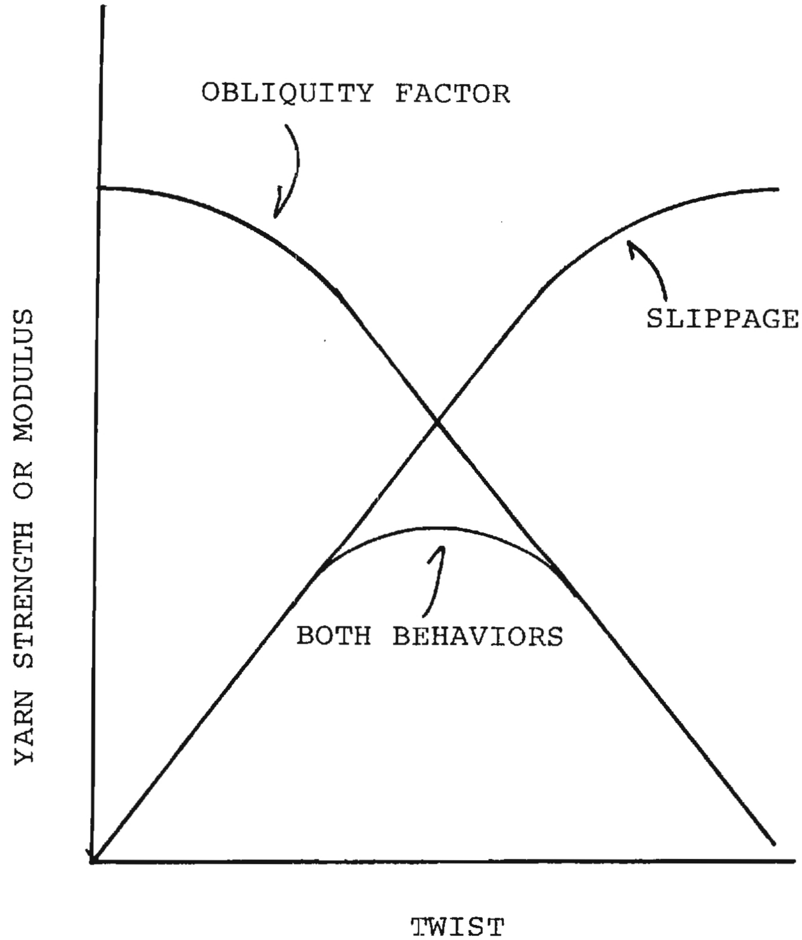
It has long been known that as yarn twist is increased, yarn strength rises to a maximum value at optimum twist and then falls. The traditional explanation of this in terms of a combination of slippage and breakage of fibers is illustrated in Figure 1.13. At zero-twist, there is no strength because the fibers merely slide over one another. The falling portion at high twists is clearly due to fiber obliquity in the yarn and is similar to the behavior of filament yarns. That is yarn strength is proportional to the $\cos^2\theta$ where θ is the helix angle of the surface fibers. The rising portion can be interpreted as a region in which the resistance to slippage increases, and the proportion of fibers which slip rather than break gradually decreases, as the gripping due to twist increases.

The modulus of a staple yarn is also affected by inter-filament friction and fiber obliquity. That is, the yarn appears to be extremely compliant at low twist levels due to the slipping of fibers past each other during yarn loading. Increasing twist serves to reduce this slippage however at the same time the yarn modulus drops by the second power of the $\cos\theta$.

A derivation of this behavior is presented in Appendix C. The modulus due to fiber obliquity is also presented in Figure 1.13. From this argument it can determined that twist

FIGURE 1.13

STAPLE YARN PROPERTIES VERSUS YARN TWIST



causes yarn modulus to have a value which is significantly lower than might be expected from a continuous filament yarn.

For this reason, it was decided very early in the program that an alternative to a twisted staple yarn should be sought. Accordingly, twistless bonded yarns appeared to be the solution for overcoming the fiber obliquity dilemna. In these twistless yarns the fibers would be gripped not by frictional forces but instead by adhesive bond forces. Fiber-to-fiber load translation would be affected not by frictional forces but instead by adhesive bond forces. Fiber-to-fiber load translation would be across an adhesive bond. A further advantage to this approach would be that during weaving, where moderate strains are imposed on the yarn, the yarns would be relatively compliant since the modulus of the adhesive (assumed to be lower than the fibers) would govern the yarn modulus. Moreover, after weaving and subsequent dissolving or pyrolysis of the adhesive, the normal forces provided by the crossover of yarns in the fabric would supply the necessary frictional forces to eliminate fiber slippage. The fabric could then be used as a composite substrate and would provide the composite with aligned fibers, a necessary condition for high translation of fiber modulus to composite modulus.

Towards the objective of manufacturing a twistless bonded yarn, a device was developed to consolidate the web into a linear strand. This device, shown in Figure 1.14, has a V-shaped groove covered with a tubular knitted endless belt on which the

CONSOLIDATION DEVICE

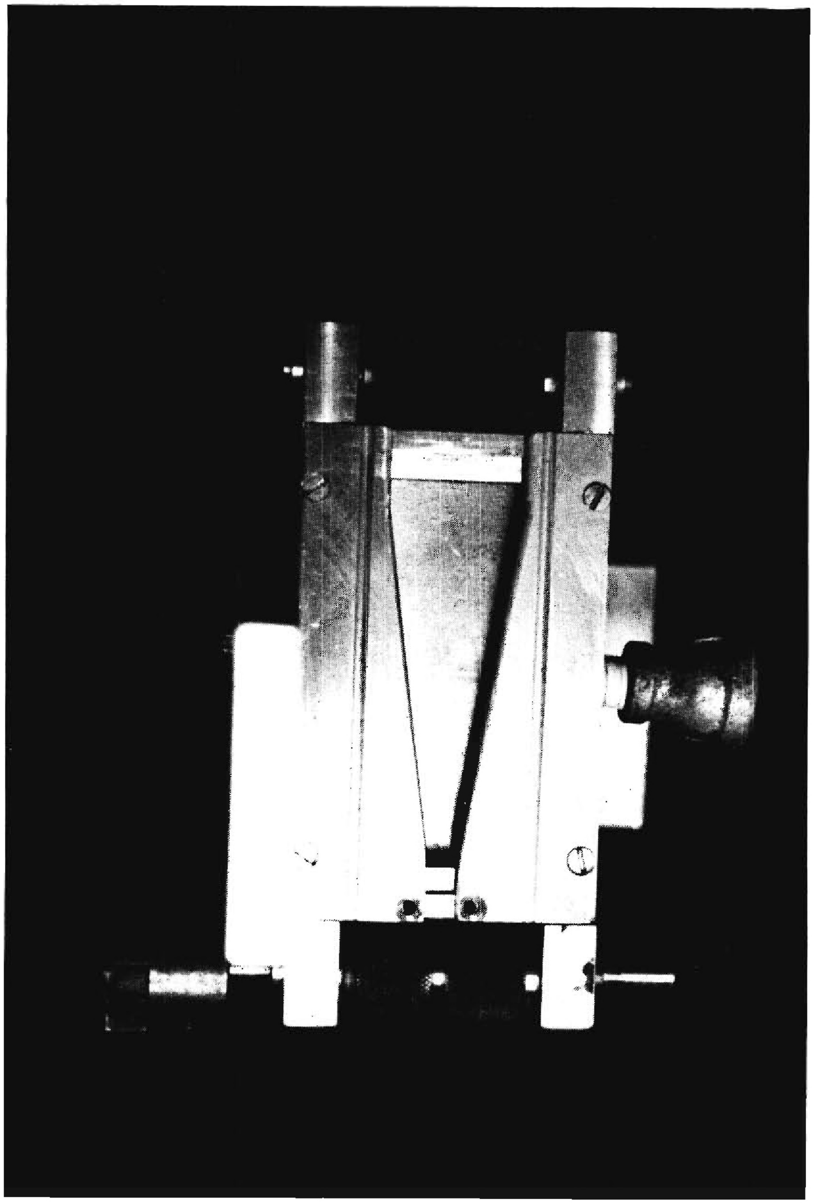


Figure 1.14 a

CONSOLIDATION DEVICE AT WORK

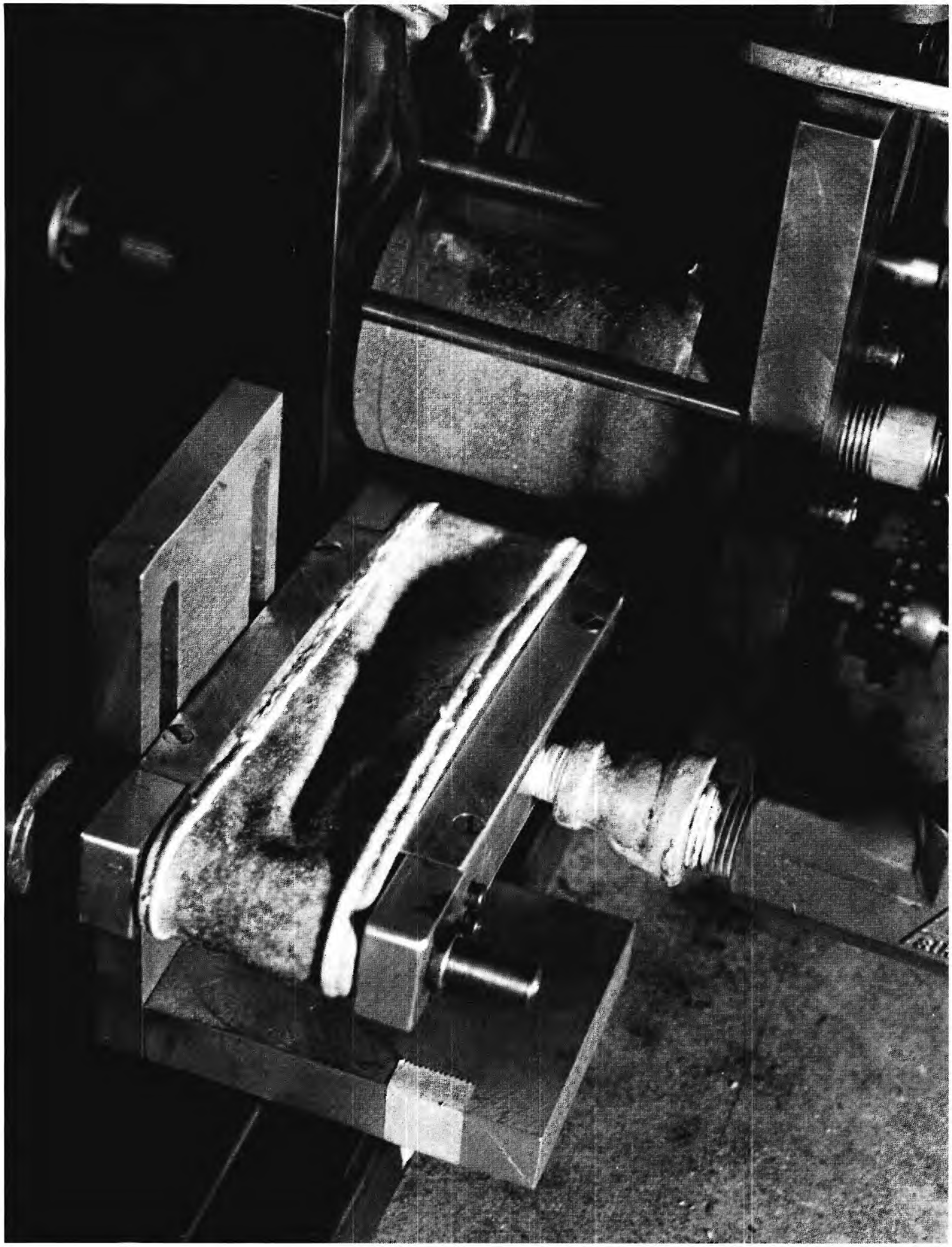


Figure 1.14 b

web is layed. The attraction of the web to the belt is a slight differential pressure supplied by a vacuum blower. This consolidation device works well and provides a moderately continuous linear assembly.

However again there is a problem with regard to keeping the assembly continuous. Drafting waves manifested during alignment and attenuation and several times the system failed due to an inadequate supply of fiber at the consolidation device. This phenomena precluded the possibility of making twistless bonded yarns since the application of adhesive onto a thin assembly would not be feasible.

As the web was delivered by the vacuum rollers, it was noted that one could hand twist this web and make a coarse yarn. Moreover, when the yarn was allowed to relax and self ply, that is twist upon itself, a coherent relatively uniform structure was formed. Following this simple experiment, a device was fabricated which twisted and pulled the yarn away from the vacuum rollers. Figure 1.15 illustrates this device. This form of twisting is called mule spinning. At one time, many staple fiber yarns were manufactured on mule spinning frames. However, after the higher production ring spinning system was invented, mule spinning lost its popularity. Mule spinning still finds application when either fine, weak or brittle fibers must be spun.

A photograph of a fabric made from a set of mule spun yarns made from pre-oxidized pitch fibers is presented in Figure 1.16.

MULE SPINNER

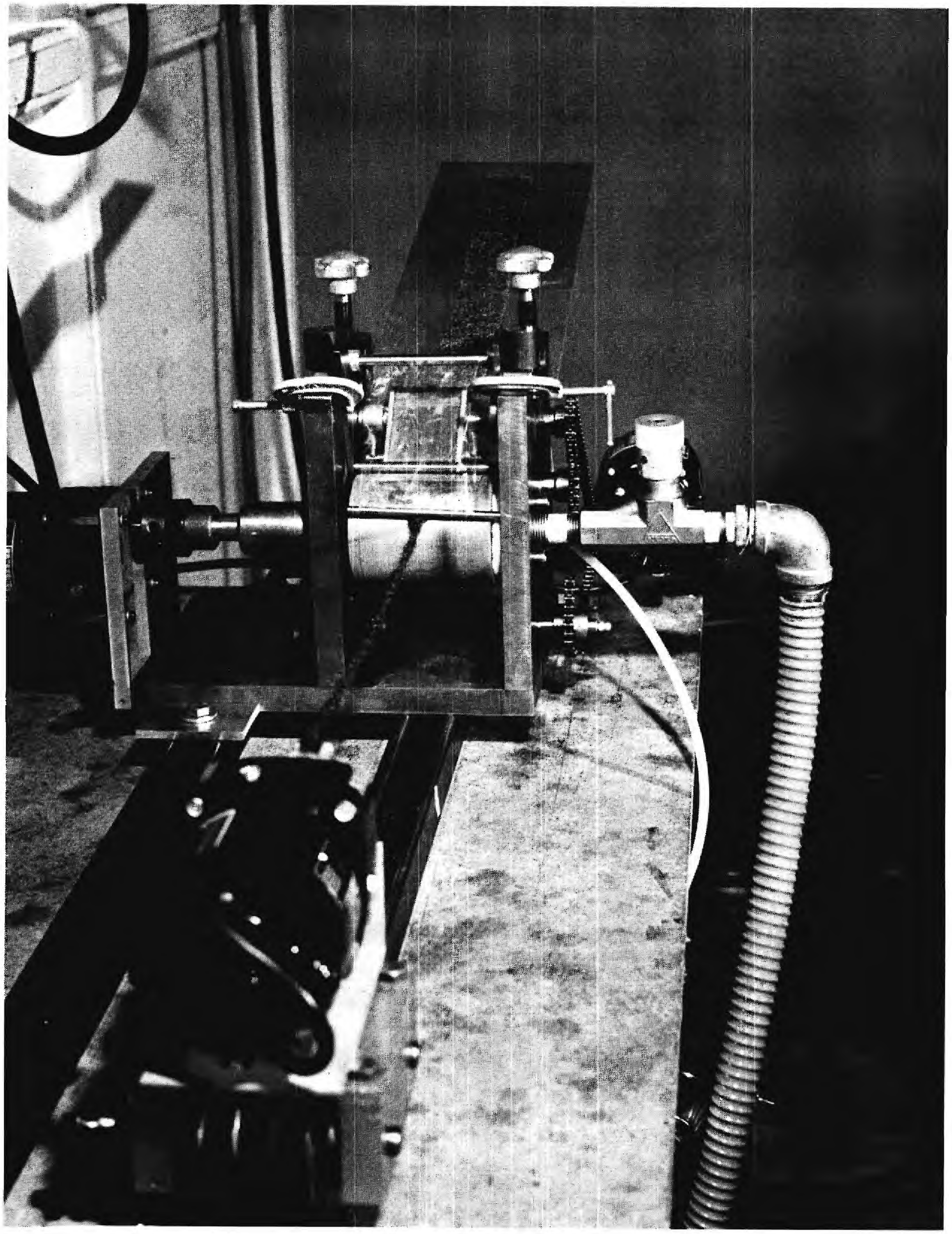


Figure 1.15

FABRIC MAT FROM PITCH-BASED
CARBON FIBER

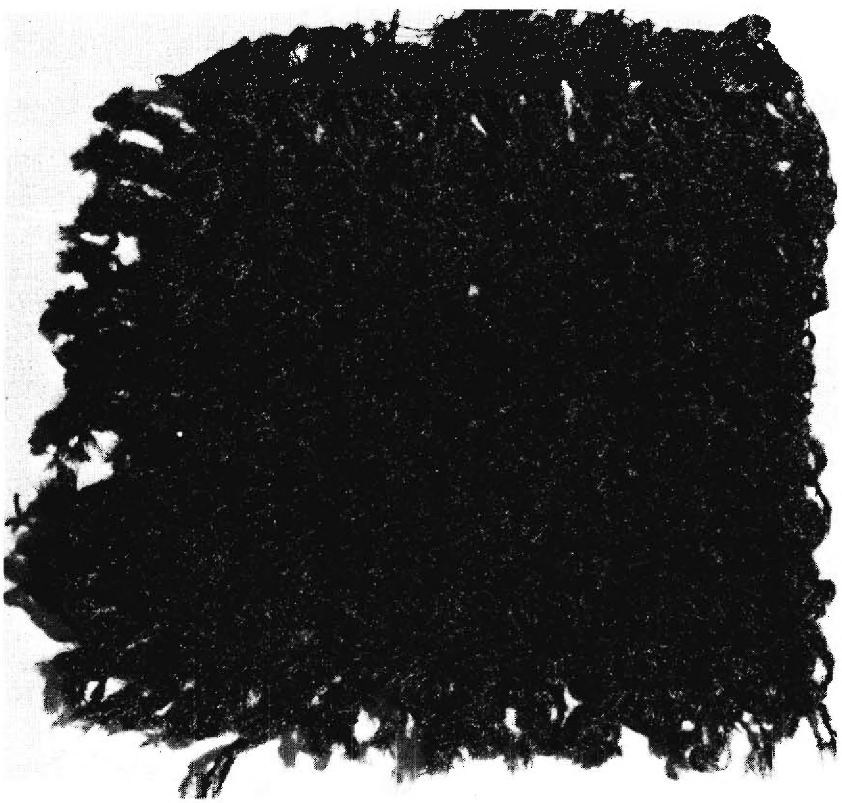


Figure 1.16

This fabric was carbonized after weaving in Greenville. Again the nonuniformity of the yarns due to drafting waves is readily observable.

During the duration of this project several other techniques for manufacturing yarn were examined. One of these techniques made use of two counter-rotating vacuum cylinders which were set to roll the fiber into a yarn (see Figure 1.17). That is the fibrous material would roll while it was pulled from the grove formed by the position of the roller surfaces. This technique did not prove to be successful.

Another technique for fabricating yarn involved the co-spinning of pitch fiber with cotton. This was accomplished at the U.S. Department of Agriculture Southern Regional Research Center (SRRC). SRRC developed an integrated yarn processing system for manufacturing yarns from loose tufts of fiber. A schematic illustration of this device is presented in Figure 1.18.

Fibers enter the system at position S. The fibers are then opened and aligned by mechanical working as they proceed to position Y. Here the fibers move across a smooth truncated conic surface into the rotor of a unique SRRC- design open-end spinner (Z). The fibers are then removed in the form of yarn by virtue of the fact that one end of the yarn is rotating with respect to the other end and this linear fibrous assembly has a forward velocity.

The device designed at Georgia Tech was interfaced at Position Y with the SRRC device and pitch fibers were co-spun

Figure 1.17

Rolling Fibers Into Yarn

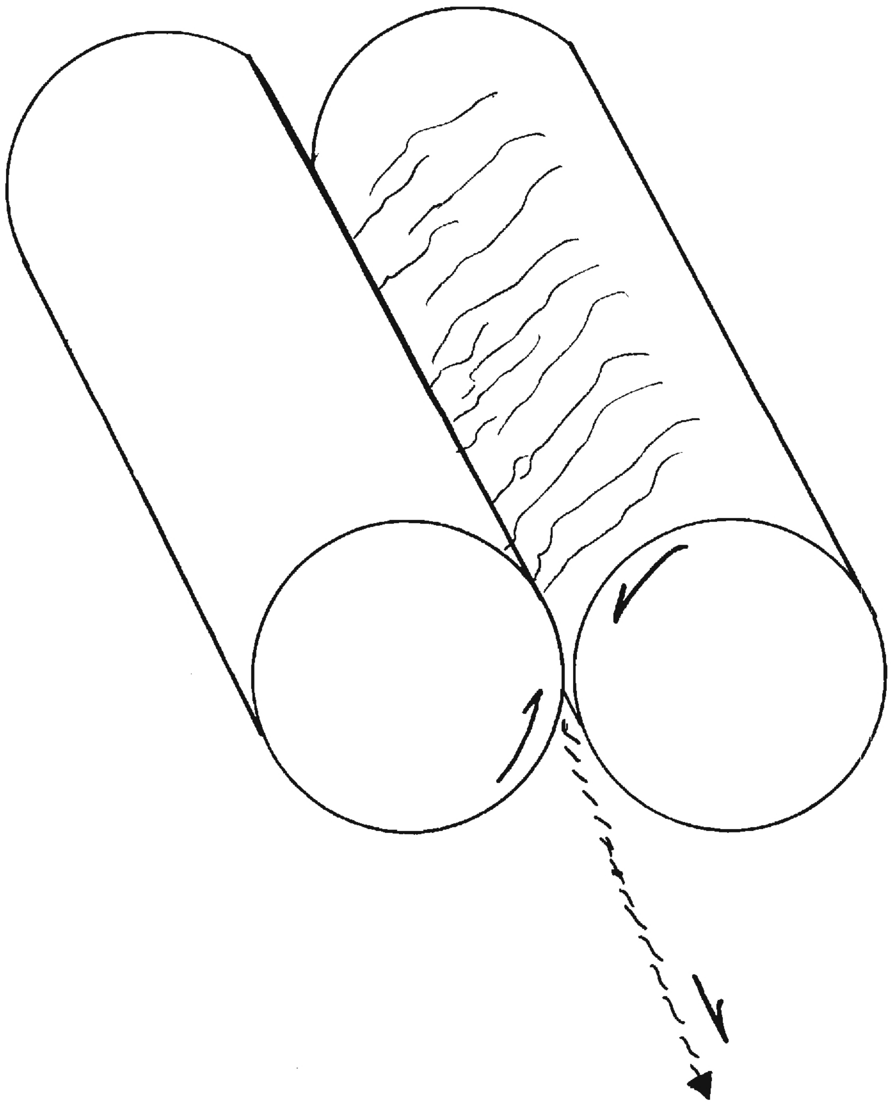
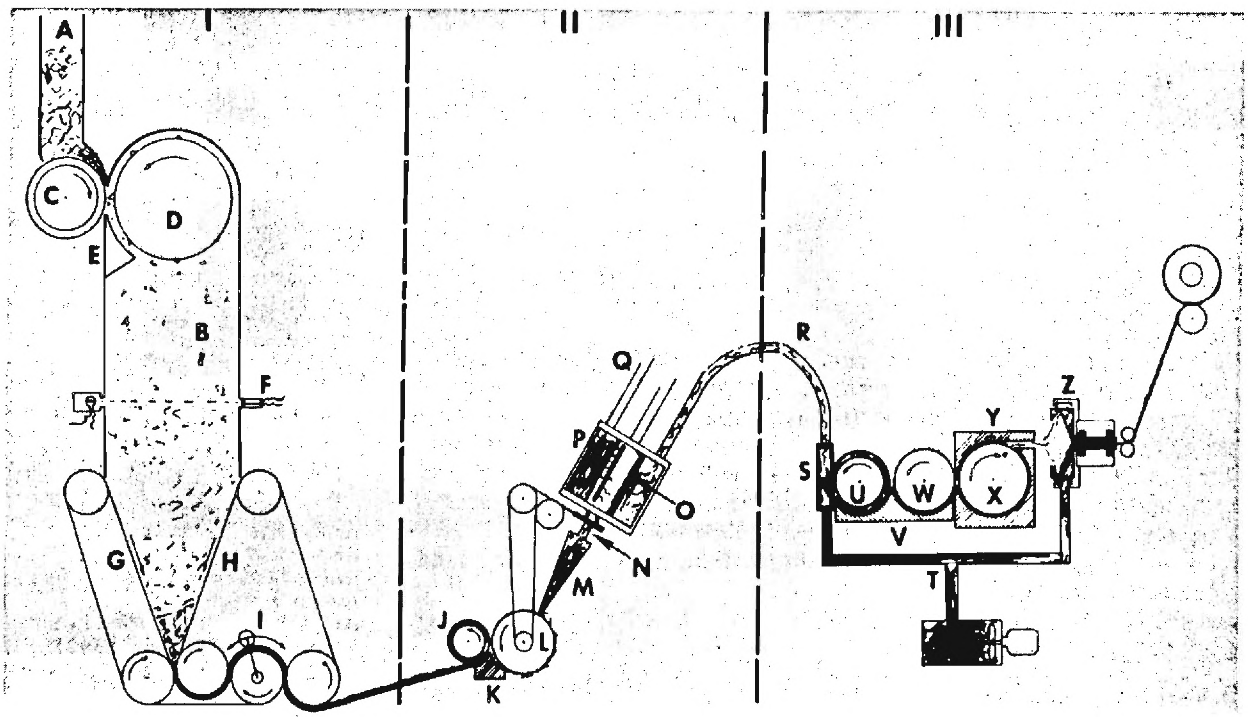


Figure 1.18

SRRC SYSTEM



successfully with cotton fibers. Cotton was chosen as the other component of this yarn since SRRC has significant experience with this fiber. It was anticipated that if this system proved effective, a component which would pyrolize during the pre-ox carbonization step would be used in place of the cotton.

A photograph negative of the yarn is presented in Figure 1.19. The white fibers represent pre-oxidized pitch. The cotton fibers do not appear since the co-spun yarn was photographed in a solution in which the refractive index was equal to the cotton refractive index.

The disadvantage to this system was the limit of pre-oxidized fiber volume fraction. The highest volume fraction measured was only 30%. Therefore, while this system of co-spinning was feasible it was readily apparent that significant modification of the SRRC and Georgia Tech system would be necessary for further development.

1.6 Web Manufacturing

The alignment and attenuation device can be used effectively to orient random carbon mat. The resulting aligned assembly can then be layered upon other layers of aligned mat until a uniformly thick structure is fabricated. Subsequent to fabrication, the material can be treated with a thermoplastic resin or thermoset resin. From this structure a resin matrix composite can be developed.

Photographs of an aligned web and the corresponding unaligned web were presented in Figure 1.5. The photograph of

Figure 1.19

PITCH/COTTON CO-SPUN YARN

(PITCH FIBERS SHOWN IN WHITE,
COTTON FIBERS INVISIBLE)

the aligned web clearly illustrates fiber alignment and the thin spots resulting from drafting waves. However, as stated before, the negative effect of the thin spots on composite modulus and strength can be minimized by layering or doubling.

A broad series of experiments was conducted in which the effect of surface speed ratio, and the effect of pre-attenuation was determined. Pre-attenuation is accomplished by using a set of nip rollers, such as those illustrated in Appendix A, to feed the mat to the nip rollers directly behind the vacuum roller. The processing conditions for this set of experiments is provided on Table 1.3. It is important to note here that all of the fibers processed in these experiments were carbonized.

Figure 1.20 serves to illustrate the effect of changing attenuation ratio (vacuum roller speed/nip roller speed) with one set of nip rollers. Examination of these illustrations shows that as draw ratio increases, alignment increases as does the formation of drafting waves. This behavior follows that which is expected when processing fibrous assemblies with a large distribution of fiber lengths.

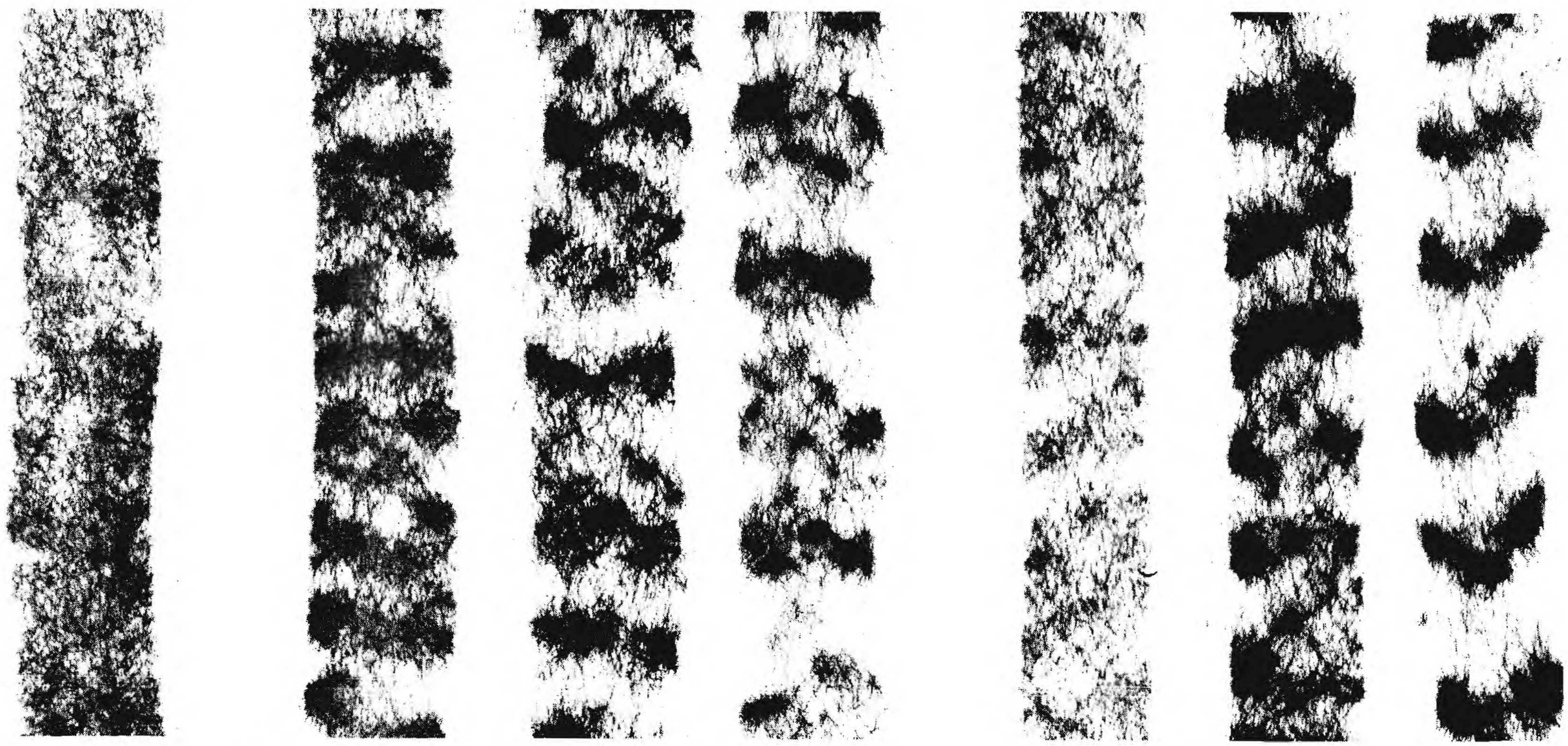
Accordingly an attenuation of 5.0 was determined to give the best aligned mat, i.e. minimal drafting waves and good alignment. All mat which was later fabricated into composites was processed at this attenuation ratio.

The effect of pre-attenuation is provided also by the illustrations in Figure 1.20. Again, alignment and

Figure 1.20

UNALIGNED MAT AND ALIGNED WEBS

A B C D E F G



UNALIGNED | RATIO 3 | 5 | 7 | RATIO 3 | 5 | 7

ONE NIP ROLLER

TWO NIP ROLLERS

Table 1.3

Various Process Settings to Specify Degree of Orientation in Longitudinal Direction

A - Unaligned Mat

Sample	Mat Thickness, Inches	Surface Speed Nip Roller 1, cm/sec.	Surface Speed Nip roller 2, cm/sec.	Vacuum Roller	Draw Ratio
B	0.038	0.22	X	0.66	3
C	0.035	0.22	X	1.10	5
D	0.040	0.22	X	1.54	7
E	0.041	0.22	0.18	0.66	3
F	0.040	0.22	0.18	1.10	5
G	0.040	0.22	0.18	1.54	7

occurrence of drafting waves increases with increasing draw ratio.

The use of pre-attenuation does not appear to have a significant affect on alignment and attenuation.

CHAPTER 2. COMPOSITE FABRICATION AND TESTING

2.0 INTRODUCTION

In this section of the final report, the results of fabrication of the aligned fibrous webs into polymeric composites will be described and discussed.

It should be recognized that the primary purpose of this composite study was to demonstrate the relative improvement in the degree of orientation of fibers after processing in our alignment process vis-a-vis the average orientation in the as-produced random mat. Two methods were considered for achieving this objective. One method involved the adhesive bonding of mats (aligned and random) by commercially available textile adhesive systems (as used, e.g., in producing chopped strand glass mat) and subsequent determination of the mat breaking strengths at angles of 0°, 45°, and 90°. The second method which was adopted, and investigated more extensively, was the fabrication of polymeric composites from aligned and random mats and the determination of the modulus of elasticity (along the principal fiber axis, for the aligned mat).

In the second method, after initial investigations with thermoplastic phenoxy resins, as developed by Union Carbide, a decision was made to employ epoxy or an unsaturated polyester resin as the matrix for the carbon fiber mat composites. It was felt that information regarding alignment, in terms of modulus measurements, could be achieved with the thermosetting resins as reliably as with the phenoxy system and that the possibility for enhanced composite results, in terms of tensile strength, might result if better resin-fiber bonding were achieved. In other words, we hoped to achieve our primary objective of demonstrating and determining the degree of alignment in our processed mats while generating additional useful data regarding the potential mechanical properties of composites with conventional thermosetting resin systems.

In order to set the stage for the discussion of our results, a brief review of the theory and experimental reports of similar studies will be undertaken.

2.0.1 Theory of Fiber Reinforcement--and Practice

The stiffness and strength of fiber-reinforced plastics are functions of the fiber properties and the quantity of fiber incorporated. In a composite composed of continuous, uniaxially aligned fibers its properties in the direction of fiber alignment may be estimated from the properties of the components by the simple law of mixtures rule:

$$E_c = E_f V_f + E_m (1-V_f) \quad \text{note: (assuming no voids)} \tag{2.1}$$

$$\sigma_c = \sigma_{uf} V_f + \sigma_m' (1-V_f) \tag{2.2}$$

where E_c, E_f, and E_m are the moduli of the composite, fiber, and matrix respectively; σ_{uf} is the fiber fracture stress, σ_m' is the stress in the matrix at the fracture strain of the fiber (assuming that the fiber is more brittle than the matrix); and V_f is the total fiber volume fraction.

In practice, equation (2.1) gives a reasonable prediction at very low levels of composite strain, but becomes increasingly optimistic as strain increases. Equation (2.2) has many limitations and is particularly difficult to apply where fibers are discontinuous, are not uniaxially aligned, and for thermoplastic matrices where severe embrittlement can occur.

2.0.2 Critical Length

When short fibers are present, stress transfer to the fiber occurs by shear at the fiber-matrix interface. The stress in the fiber builds up from zero at each end and, when the fiber is long enough, reaching a certain constant value. By progressively increasing the stress on the composite, this value will be raised to a level where either the fiber will break in tension, or the matrix will fail by shear flow, or rupture of the fiber matrix bond.

When a fiber is shorter than a certain "critical length", the stress cannot build up to a value sufficient to cause fiber fracture and shear failure may occur instead. The concept of a minimum fiber length arises because the actual ends of the fiber cannot support a tensile load. The load builds up from the ends of a fiber, as shown in Figure 2.1.

The critical length, L_c, is given by equation 2.3.,

$$L_c = \frac{\sigma_{uf} d}{4\tau} \tag{2.3}$$

where σ_{uf} = fiber fracture stress

d = fiber diameter

τ = shear stress at the interface

In an ideal system it has been calculated that the fiber length in a composite should be of the order of 5 L_c for optimum performance.

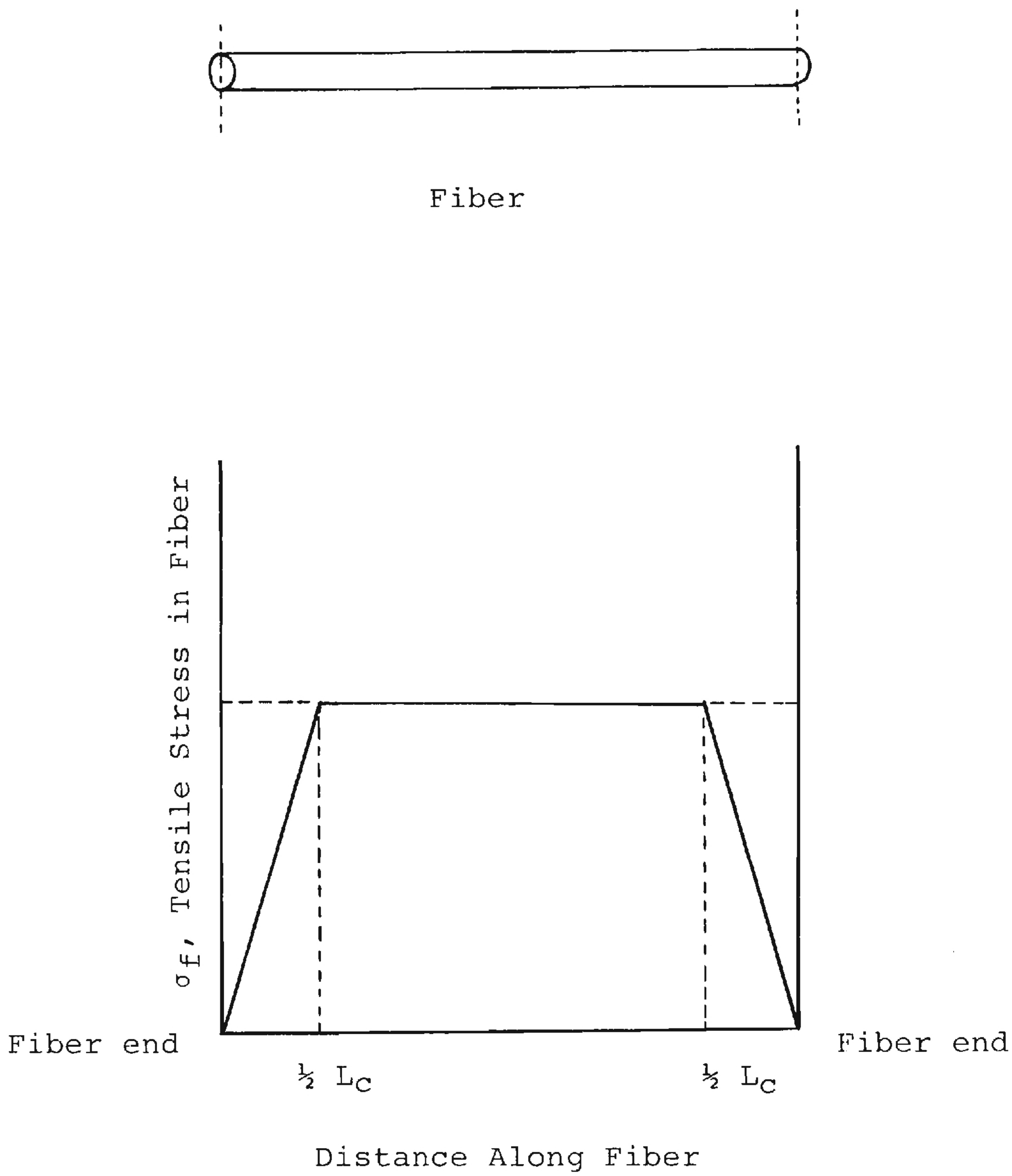


FIGURE 2.1. Stress Distribution on a Fiber in a Matrix

From industrial practice it is known that, for a given fiber diameter, the efficiency of reinforcement does begin to drop off rapidly below a certain length. Reinforcement efficiency is that proportion of the maximum mechanical properties of a given fiber which can be transferred or utilized within a composite. A reinforcement efficiency of unity is equivalent to total use of the fiber length for transfer of stress. This case is only approached for a continuous fiber in an unkinked condition, which initimately bonds to the matrix. Deviation from unity is due to the fact that, as seen in Figure 2.1., there is no stress transfer at the ends of fibers and, for a given distance from the ends of the fiber, only partial stress transfer is attained. One method of calculating the reinforcement efficiency index, η, is to employ the equation,

$$\eta = \frac{(L - 2x)}{L} \qquad (2.4)$$

where "L" is total fiber length and "x" corresponds to an incremental length from the end of the fiber which is assumed not to contribute to stress transfer. For the case illustrated in Figure 2.2., "x" is taken as 0.1 inch. This means, in practice, that chopped glass fiber less than a total length of x, $(x < L)$, does not contribute to the reinforcement of the matrix. In Figure 2.2., it is shown that for chopped strand fiber mat (average diameter, 7.5 microns), the composite strength of a laminate falls off dramatically when fibers below 0.5 inches in length are used.

Unlike composites made from mat of chopped strand glass fibers, where all fibers may have the same length, the composites

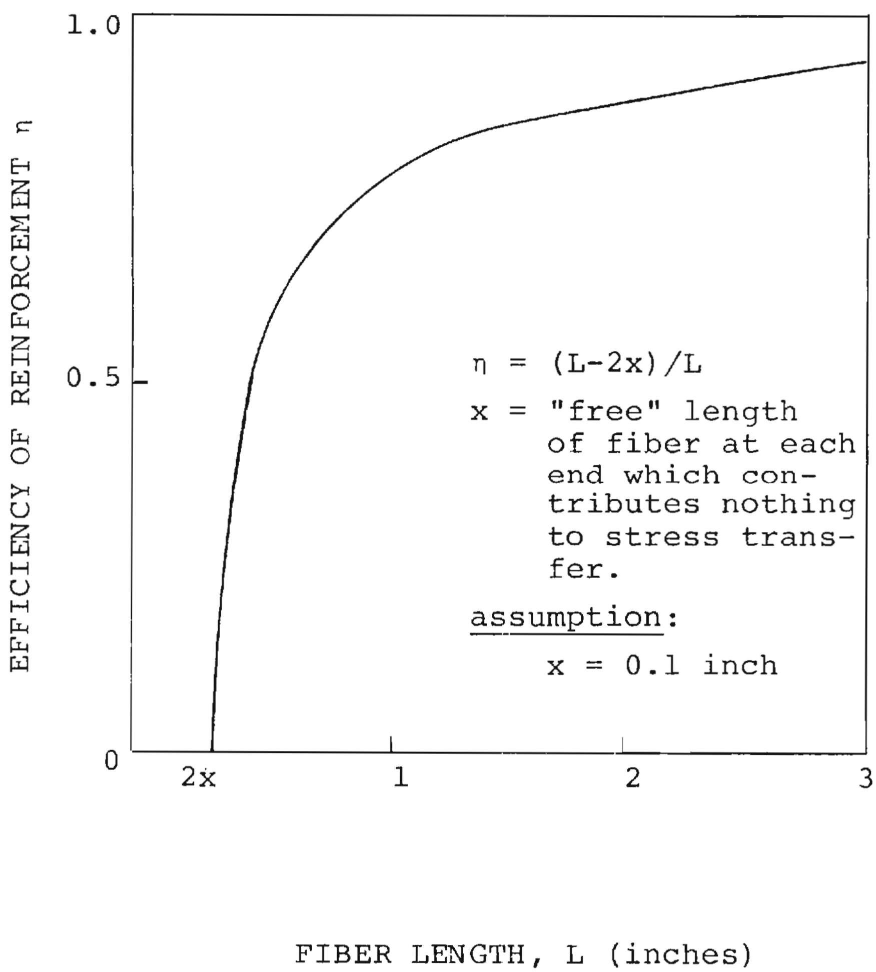


FIGURE 2.2. Reinforcement Efficiency Index vs. Fiber Length for Glass Chopped Strand Mat-Polyester Composite.

made from the Union Carbide mat possess a wide range of fiber lengths. The levels of stress for fracture of the composites made from the pitch-based, staple mat may be expected to vary more widely than those of similar composites made from fibrous reinforcements of uniform lengths, therefore.

2.0.3 The Aspect Ratio

In fact, model studies and theoretical considerations have established that it is not absolute fiber length which is the decisive factor in the efficiency of reinforcement of composites but, rather, the length-to-diameter ratio (L/d) which is most critical.

The desired value of the aspect ratio, L/d, depends on the stress to be carried in the fiber, the shear modulus of the matrix, and the interfacial shear strength between fiber and matrix. It varies, therefore, with the system under consideration. One self-consistent analysis calculated that an aspect ratio of 300-to-1 or more is required for thermosetting resins with high strength fibers and that an L/d of 30/1 is adequate for coarse fibrous asbestos-reinforced systems. Aspect ratios as low as 20/1 are useable in reinforcement of thermoplastics which must flow smoothly during molding.

While available theory does have the apparent advantage of self-consistency, theoretical analysis does not always provide an accurate description of actual performance. For example, one approach has predicted an L/d ratio of 60/1 for effective reinforcement of polyester resins by chopped glass fibers. In the previous paragraph, a value of 300 or more is specified. Reference to Figure 2.2, and an analysis of those results demonstrates that an aspect ratio of at least 1700/1 is necessary for the system.

Grading

While random mats of glass fibers with consistent lengths can be achieved by controlled, reproducible chopping of continuous roving and dispersion, other discontinuous fiber systems are inherently diffuse in terms of fiber diameter and fiber length. The staple carbon fiber mat which we have investigated falls in this category, as does asbestos. Our study has not focused on narrowing the distribution of aspect ratio by control of diameter nor of length, of course. However, grading techniques have been established for asbestos and other short fibers. Dispersed particles and fibers denser than water may be separated on the basis of diameter via their surface-drag/mass ratio (e.g., the hydrocyclone). Separation by length is more difficult but some success has been achieved with rotating screen machines.

For short fibers, such as asbestos, therefore, it has been found necessary to apply a grading or sorting process in order to overcome the difficulties of poor reinforcement efficiency. Grading, followed by alignment, allows optimization of reinforcement efficiency.

Alignment

The effect of fiber alignment on mechanical properties is considerable. If fibers were randomly oriented in three dimensions their reinforcing effect has been calculated as 0.167 of that of uniaxially aligned fibers, measured in the fiber direction. If the fibers are randomly oriented in one plane only, one may derive a value of 0.375. This is the case which has been adopted to describe the build-up, multi-layer structures of aligned web which are used as reinforcements in this study.

The modulus of composite specimens, in which the fibers are oriented at a bias angle to the direction of extension, is a function of the fiber extension modulus, the transverse modulus, the shear modulus, and Poisson ratio. However, a simplified expression for modulus can be derived on the following basis. Reference is made to Figure 2.3.

$$\varepsilon_c = \frac{\Delta L}{L}$$

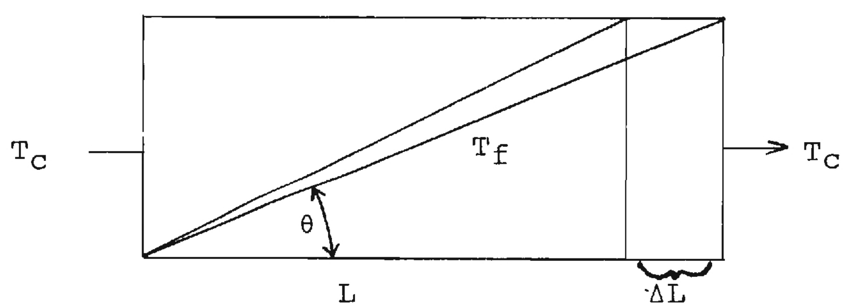


FIGURE 2.3. Simplified Composite Model

For this analysis, the mechanical properties of the resin matrix are neglected since they do not contribute significantly to the composite properties, other than in its ability to transfer load between fibers.

A load, T_c is applied to the specimen. Accordingly, the specimen is strained to a value ε_c. Now if the specimen is strained to ε_c it can be shown that the fiber strain in the lamina must be $\varepsilon_c \cos^2\theta$. Likewise the tension in the fibers is $T_c/\cos\theta$. Accordingly, fiber stress, σ_f, must be $\frac{T_c}{A_f \cos\theta}$. The total cross sectional area of the fibers can be shown as $A_c \cos\theta$. Thus we have the following relationships:

$$\varepsilon_f = \varepsilon_c \cos^2\theta \tag{2.9}$$

$$T_f = T_c/\cos\theta \tag{2.10}$$

$$\sigma_f = T_c/\cos\theta \, A_f \tag{2.11}$$

$$A_f = A_c \cos\theta \tag{2.12}$$

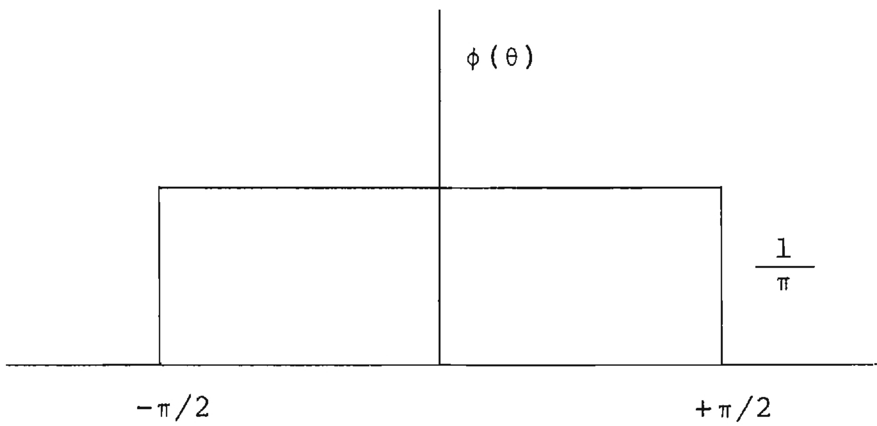
Combining these relationships we obtain:

$$E_c = E_f \cos^4\theta \qquad \text{note: assume poisson ratio} = 0 \tag{2.13}$$

where E_c = composite modulus

E_f = fiber modulus.

The specimens which are fabricated from random mat can be imagined to consist of a infinite series of lamina of different orientation. Accordingly, the probability distribution function of the orientation can be illustrated as in Figure 2.4.



$$\int_{-\pi/2}^{\pi/2} \Phi(\theta)\ d\Phi = 1$$

FIGURE 2.4. Probability Distribution Function for Random Mat Composite

This function indicates that a uniform distribution of orientation angle exists from $-\pi/2$ to $\pi/2$. The modulus is then

$$E_c = E_f \int_{-\pi/2}^{\pi/2} \phi(\theta) \cos^4\theta \, d\theta \tag{2.14}$$

and since $\phi(\theta) = \frac{1}{\pi}$

$$E_c = 3/8 \, E_f \tag{2.15}$$

On the basis of this derivation, therefore, one would expect to obtain a maximum composite modulus of 37.5% that of the modulus of the fibers in a uniaxially-oriented laminar structure for the case where randomly oriented reinforcement is used in a homogeneous matrix. (See e.g., Tsai and Pagano, Composite Materials Workshop, Technomic Publ., Stamford, Conn., p. 249, 1968).

In practice, of course, the relationship of the modulus of a unidirectional-oriented fibrous composite and that of a randomly-oriented fibrous composite can vary for many reasons. The relationship which we have derived is for an ideal system. It is useful and pertinent to our subsequent discussion to examine the experimental results of actual investigations of the dependence of modulus on fiber alignment, i.e., orientation. Table 2.1 is reproduced from a recent study by D. McNally (Polym. Plast. Technol. Eng. 8(2), 101-154, 1977).

TABLE 2.1 Random vs. Undirectional Tensile Modulus of Composites

R = Random-in-plane orientation
U = Unidirectional orientation

Matrix	Reinforcement	Orientation	Tensile Modulus GPa	R/U,%
Ionomer	Nylon 66	R	0.427	62.2
		U	0.687	
	Polyester	R	0.800	55.0
		U	1.455	
	Polyvinyl Alcohol	R	1.462	61.3
		U	2.386	
	Glass	R	2.910	45.9
		U	6.343	
	PRD-49	R	5.033	56.6
		U	8.894	
	Graphite	R	7.033	38.4
		U	18.34	
Polyethylene	Nylon 66	R	1.01	60.8
		U	1.66	
	Polyester	R	1.32	75.4
		U	1.75	
	Polyvinyl Alcohol	R	1.66	55.3
		U	3.00	
	Glass	R	3.41	36.1
		U	9.446	
	PRD-49	R	5.16	48.7
		U	10.6	
	Graphite	R	6.66	34.5
		U	19.31	
Nylon 12	Nylon 66	R	1.15	87.1
		U	1.32	
	Polyester	R	1.54	65.8
		U	2.34	
	Polyvinyl Alcohol	R	2.16	70.6
		U	3.06	
	PRD-49	R	4.17	48.8
		U	8.55	
Polycarbonate	Glass	R	3.94	52.6
		U	7.52	
	PRD-49	R	5.06	51.7
		U	9.79	
	Graphite	R	8.55	67.7
		U	12.62	

TABLE 2.1 (cont'd)

Matrix	Reinforcement	Orientation	Tensile Modulus GPA	R/U,%
Iolymethyl methacrylate	Nylon 66	R	2.26	70.6
		U	3.20	
	Polyester	R	2.65	78.4
		U	3.38	
	Polyvinyl Alcohol	R	3.94	79.1
		U	5.48	
	Glass	R	4.50	42.9
		U	10.48	
	PRD-49	R	7.79	70.2
		U	11.10	
	Graphite	R	9.58	40.9
		U	23.44	

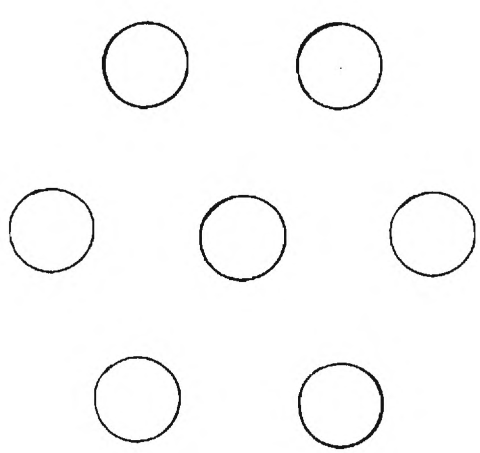
The results of this study and others have shown that the simplified derivation which we have presented incorporates numerous assumptions and effectively disregards many complex interactions during composite material stressing and failure. McNally provides an in-depth review of many authors' approaches to the prediction of modulus and other mechanical properties for random and aligned reinforced composites.

2.0.4 Volume Fraction

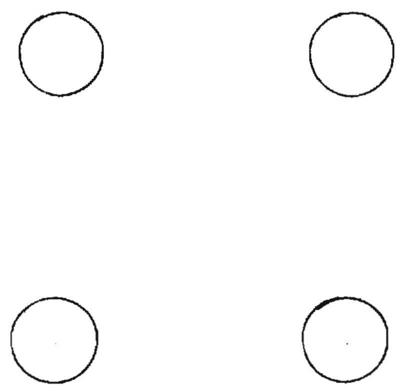
Alignment allows the maximum amount of fiber to be incorporated into a composite. The higher the loading of high modulus fibers, the higher the composite modulus, as is evident from the Rule of Mixtures.

Since the reinforcement is the dominant component of a structural reinforced plastic from the standpoint of contributing to, and establishing, an upper limit on the strength and modulus of the composite, it is desirable to incorporate a high volume of percentage of reinforcement in the composite.

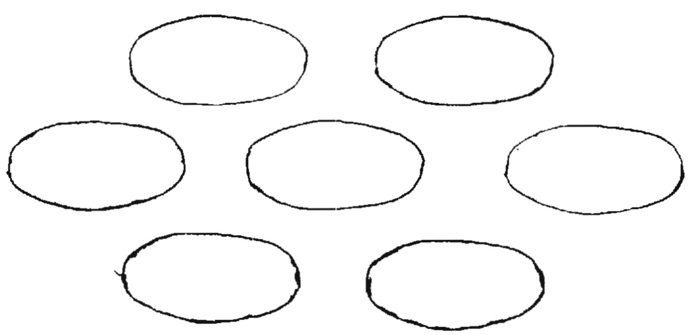
For circular cross-sectional fibers packed in a hexagonal array the maximum possible volume percent of fibers is 90.5:



For a square-packed array, the maximum possible volume percentage of fibers is 78.5:



For other cross-sectional fiber shapes, such a elliptical and others, the maximum possible volume content could even be higher:



In actual practice, however, the volume content of fibers ranges between 50 and 75%. If the fiber volume content increases much beyond 75%, the reinforced plastic becomes "resin-deficient" with a resultant decrease in interlaminar shear strength and edgewise compressive strength.

Deviations occur automatically in practice as fibers do not segregate and disperse themselves ideally, and, obviously, all fibers are not uniform in shape nor diameter. In the case of continuous fibers it essential that tensioning be applied to ensure adequate alignment. In the case of discontinuous fibers, maintenance of fiber orientation, particularly in low viscosity matrices becomes very difficult. Consolidation during fabrication by conventional processes can cause excessive breakdown of fibers with the result that only a small fraction of fiber properties are realized in the final composite.

"Misalignment" can be advantageous if the mainly aligned web can be keyed together by a small proportion of misaligned fibers, particularly if this allows enough mat strength for easy handling. This could allow a prepreg to be formed to the profile of a mold without destroying the uniformity of fiber distribution and orientation.

The achievement of high packing fractions, i.e., high fiber volume loadings, is considerably dependent on developing an appropriate molding procedure which is dependent both on the rheological and curing properties of the resin matrix and the nature or structural integrity of the reinforcement. The molding pressure depends on the degree of alignment and fiber geometry and, generally, prepregs made from short fibers require higher pressures than those incorporating an equivalent loading of continuous fibers.

2.1 EXPERIMENTAL SECTION

2.1.1 Adhesive Bonding

A short-term investigation was undertaken to determine whether adhesive bonding of mats might provide a useful, quick method for determination of an orientation/alignment index. Additionally, the study would provide an indication of the potential for improving the "handleability" of the mat for subsequent processing (analogous to glass fiber chopped strand mat).

All work was conducted on random mat and "pre-ox" fibers because sufficient quantities of aligned mat were not yet available at the time of this study.

A) Bonding of Carbon Fiber Mats

Ten resin samples, six from Borden Chemical and four from National Starch Company, were tested for use as binders on random, "pre-ox" fiber mats. Descriptions of these resins are contained in Appendix D.

The bonded fiber mats were prepared according to the following procedure: mats, 9 x 10 inches in size with a typical bulk density of 375 g/m^2 (1.25 $oz./ft^2$) were soaked in deionized water for ten minutes to wet them thoroughly. They were then sprayed with an emulsion of binder of approximately 3% solids content. (The commercial emulsions were diluted with water only and no attempt was made to introduce lubricants, wetting agents, or other additives.) An insecticide sprayer at a "fine mist" setting was used to saturate the mat and to achieve an even distribution of binder. The mats were drained for ten minutes on a wire mesh screen and were then placed into an air-circulating oven set at $120^\circ \pm 3^\circ C$ for a period of six hours. Some samples stuck to the wire screen despite deposition of a fluorocarbon release agent on the screen.

The solids content for each mat was determined by solvent extraction with benzene.

The solids content of the emulsions were determined by evaporation of the solvent in an air-circulating oven at $120^{\circ} \pm 3^{\circ}C$, after placing a representative sample of the well-stirred emulsion in a tared aluminum disk. Two determinations, which agreed within 0.5% after drying to constant weight, were made.

Emulsions were used immediately after preparation to avoid any destabilization.

Most of the mats were tested for mat strength with a Monsanto Tensometer using a 31.25 kilogram spring beam. Tests were conducted in four directions generally: 0°, 45°, 90°, and 135° where 0° is taken as the machine or belt direction during fabrication.

2.1.2 Composite Fabrication and Testing

A) Phenoxy Resin Composite

Carbon fiber resin preforms were made by impregnating the carbon fibers with solvent solution of phenoxy resin and then evaporating the resin. The preforms were then stacked and hot pressed to form the composites used for testing.

The preforms were made by the following procedure.

A solution of 7-8% by weight of Union Carbide PKHC in a 4:1 mixture of MEK and Toluene was made by slowly adding the resin to the solvent while stirring continuously. The mixture was stirred over night to insure that the resin was completely dissolved. To impregnate the fiber with the phenoxy resin, a sandwich consisting of a light (.3 oz./sq.yd.) Cerex sheet, carbon fiber mat, and a heavy (2 oz./sq.yd.) Cerex sheet was placed on an expanded metal support. The resin/solution was uniform by pouring over the assembly. The heavy Cerex sheet was replaced with a sheet of release paper and the lay-up worked by hand to distribute the resin uniformly in the fiber mat. The lay-up was then allowed to drain for several minutes to remove excess resin. A flat metal plate was then placed on top of the lay-up, the whole assembly turned over and the expanded metal support was removed and replaced by a sheet of release paper. This assembly was then heated in an oven for one hour at 110°C to evaporate the solvent. The resultant fiber mat impregnated with resin, called preforms, were used to fabricate specimens for the mechanical tests.

To fabricate the test specimens, 20 preforms, 2" x 4", were stacked and pressed to 0.16 inch stops at 175-200°C in a hydraulic press. Test specimens, approximately ½" x 2", were cut from these coupons and tensile tested in an Instron Universal tester to determine Young's modulus. Composites were fabricated from non-aligned pre-ox fibers and aligned pre-ox fibers which were subsequently carbonized.

B) Epoxy Resin Composites

Shell epoxy resin Epon 820 with DDS (diaminodiphenyl-sulfone hardner and BF_3-MEA (BF_3-monoethylamine), as an accelerator, was used to make carbon fiber composites.

Two different formulations were used: (1) 20 phr of DDS and, (2) 20 phr DDS with 1 phr of BF_3-MEA. The resin was heated to approximately 300^{o}F and the DDS stirred in until dissolved. If BF_3-MEA was to be used, the mixture was cooled to about 195^{o}F where the BF_3-MEA was added and stirred until dissolved. The mixture was then dissolved in approximately 100 parts acetone to 120 parts resin mixture. This solution was used to impregnate the carbon mats by methods similar to that described in the section on the phenoxy resin composites. The impregnated mats were pressed with and without shims in a heated platten press at 350^{o}F. Because of the low viscosity of the resin at the curing temperature of 350^{o}F, excessive resin bleed caused the resultant composites to be unsatisfactory due to extreme washing of the carbon fibers. To try to contain the resin and control bleed-rate, a "leaky" mold was used to press some specimens; however, the same problem of excessive resin-bleed, which resulted in poor composites, was encountered.

A vacuum bag procedure was tried where the composite was cured at 350^{o}F under vacuum of approximately 20" of Hg. As before, the low viscosity of the resin caused excessive resin loss and an unsatisfactory composite. The results of these trials are summarized in Table 2.2. Because of the fabrication difficulties encounterd, it was decided to try a room temperature curing polyester resin.

TABLE 2.2. Epoxy-Composite Fabrication

	Epon 828	DDS	Acetone	BF_3-MEA	Temp.	Pressure	Technique	Comments
1)	100 pts	20 pts	100 pts	0	350°F	4-7 tons	Press	No shims were used. 10 ml of solution was applied. When heated, resin ran all over the platens. The mat was pressed between mylar sheets and post-cured for 2 hrs. at 400°C in a circulating oven. It warped since the mylar sheets were left on.
2)	100 pts	20 pts	100 pts	0	350°F	4-7 tons	Press	0.012" shims used, and only 2 ml of solution. Mat appear-ed resin poor after post-curing as above. Resin still ran over platens.
3)	100 pts	20 pts	100 pts	0	350°F	4-7 tons	Press	0.012 " shims used, only 1 ml of solution. Mat extremely resin poor, but not so much ran over the platens.
4)	100 pts	20 pts	100 pts	0	350°F	4-7 tons	Press	Wrapped in aluminum foil in order to attempt to contain the resin. Used 5 ml of resin and pressed with an aluminum bar on top, sealed inside the foil. Did not con-tain the resin.
5)	100 pts	20 pts	100 pts	1 pt	350°F	28 mm Hg	Vacuum Bag	Used over 9 g resin

TABLE 2.2. (cont'd)

5) (cont.)							(after evaporation of acetone) pressed with Al bar on top. Mat did not press down enough and resin did not spread out enough. May have set too fast.
6) 100 pts	20 pts	100 pts	1 pt	350°F	28 mm Hg	Vacuum Bag	Used only about 4 g resin. Pressed in vacuum bag only, with fiberglass pads to absorb excess resin. Did not press down--resin apparently was set before pressing.
7) 100 pts	20 pts	100 pts	0	350°F	4 tons	Press with mold	Mold had gaps through which resin and mat squeezed out while being pressed. Used 0.025" shims.
8) 100 pts	20 pts	100 pts	0	350°F	4 tons	Press with mold	Mold partially welded to seal gaps. Used too thin shims, 0.037" and most of mat squeezed out while being pressed.
9) 100 pts	20 pts	100 pts	1 pt	350°F	4 tons	Press with mold	Used up to 25 tons pressure, but did not press down. Mat was set up before pressing.

TABLE 2.2 (cont'd)

10) 100 pts	20 pts	0	0	350°F	4 tons	Press with mold and rubber gasket	Pressure applied until resin began to bleed. Very little pressure - resin ran all over. Mat resin poor. (No shims because of rubber mat)

C) Polyester Resin Composites

Reichhold Chemical Polylite 33-031 polyester resin with MEK perioxide curing agent was the resin system chosen. This resin is a general-purpose resin designed for hand lay-up and promoted for room temperature cure.

The vacuum bag technique was chosen as a specimen fabricating technique. The vacuum bag was layed out. Then the resin was mixed with 1% MEK peroxide hardner. The resin mixture was uniformly poured over the carbon fiber mat, the impregnated mat was placed in the vacuum bag, the bag sealed and connected to a vacuum source. The composite was cured, under vacuum, at room temperature for at least one hour. After removal from the vacuum bag, the sample was post-cured for approximatly sixteen hours at 77°F.

The composite produced by this method and with the polyester resin appeared to be suitable for the tensile modulus tests. Therefore, several composites approximately 2" x 9" were fabricated from unaligned carbonized mat and aligned carbonized mat.

Tensile specimen ½" x 8" were cut from these composites for determination of Young's modulus.

D) Testing

The tensile tests were performed using a Instron Tensile tester. Elongation of the phenoxy composite specimens was measured with a 10 mm gage length Instron strain gage extensiometer. The elongation of the polyester resin composites was measured with a one-inch gage length Instron strain gage extensiometer. The Instron has a recorder which records load on the x-axis and elongation on the y-axis. The cross-sectional area of the specimen was used to convert the load to stress. The elongation was converted to strain by dividing the elongation by the gage length and Young's modulus was determined by calculating the slope of the resultant stress-strain cure.

To compare the modulus of composites with aligned fibers with composites with unaligned fibers, the modulus values must be normalized to the same fiber volume fraction. To be able to do this, the volume fraction of each composite test was determined. Two methods were used to determine the fiber content of the test specimens. The first method consisted of digesting a weighed composite sample in a mixture of 25% nitric acid and 75% dimethylsulfoxide for 72 to 84 hours at 220°F. This digestion dissolves the resin but leaves the carbon fiber unaffected. After the resin was dissolved, the carbon fibers remaining were washed, dried and weighed. The fiber volume fraction was then calculated using the following equation:

$$V_f = \frac{\rho_f W_f}{\rho_r W_f + \rho_f W_r}$$

where V_f = volume fraction fiber

ρ_r = resin density

ρ_f = fiber density

W_r = weight of resin in digested sample

W_f = weight of fiber in digested sample

The fiber density was determined by the "sink-float" method in a mixture of dibromoethane and ethyl alcohol. The density of cast resin was calculated from its weight in air and in water.

Because of the long length of time required to digest the resin in the composite samples, another quicker method was used to determine fiber content. A weighed sample, in this method, was placed in a muffle furnace at 400°C for at least four hours. At this temperature, the resin is oxidized and removed with essentially no loss of carbon fibers. The sample is then removed from the muffle furnace, cooled and weighed. The volume fraction of the fiber is calculated using the same expression as for the digestion procedures.

2.3 RESULTS AND DISCUSSION

2.3.1 Adhesive Bonding

Table 2.3. summarizes the mat breaking strength data for each of the ten adhesives systems which were investigated.

The strength data suggests that the mat is reasonably random in orientation with, perhaps, a slight unexpected bias at 45°. Zero (0°) orientation is taken to represent the machine or belt direction in the Greenville plant.

The best adhesives appear to be Borden 2140 and National Starch 2211. A microphotograph at 200X magnification of Borden 571-bonded mat is shown in Figure 2.5. The latex thoroughly covers the fiber surfaces and preferentially accumulates at cross-over points of the fibers. The film-forming properties of the latex is evident. The poor results achieved with vinyl chloride and styrene-butadiene latexes, particularly in view of the relatively high binder content, discounts their usefulness as potential mat binders. (Note--glass chopped strand mat is unlikely to contain more than 5% binder.)

The results in general, as compared with the adhesive

TABLE 2.3. Strength vs. Direction: Adhesive-Bonded Mats

EMULSION	TYPE	% SOLIDS, EMULSION	% SOLIDS, MAT	BREAKING STRENGTH (KG/LBS.)			
				0°	45°	90°	135°
Borden 571	Vinyl Acetate Homopolymer, large particle size	8.14	46.3	11.0 (24.2)	-	-	-
Borden 571	Vinyl Acetate Homopolymer, large particle size	3.60	19.8	3.2 (7.0)	3.8 (8.4)	3.1 (6.8)	4.0 (8.8)
Borden 2140	Vinly Acetate Homopolymer, small particle size	3.85	15.6	0.5 (1.1)	0.7 (1.5)	0.4 (0.9)	- (-)
Borden 2151	Vinyl acetate--acrylic co-polymer	3.25	18.1	2.0 (4.4)	1.6 (3.5)	1.9 (4.2)	2.2 (4.8)
Borden 2445	Styrene-Buta-diene Copoly-mer Latex	2.60	14.4	0.3 (0.7)	0.2 (0.4)	0.3 (0.7)	0.3 (0.7)
Borden 2607	Vinyl Chloride Copolymer Latex	3.06	8.7	0.4 (0.9)	0.1 (0.2)	0.2 (0.4)	- (-)
Borden 2618	Plasticized Vinyl Chloride Copolymer	3.35	12.55	1.0 (2.2)	- (-)	- (-)	- (-)
National Starch 1014	Vinyl Acetate Homopolymer, small particle size	3.14	-	0.3	0.0	0.1	0.1
National Starch 1048	Vinyl acetate	3.38	-	2.1	1.9	2.2	2.0
National Starch 2211	Vinyl acetate copolymer	3.25	-	2.2	4.4	2.0	-

TABLE 2.3. (cont'd)

National Starch 2211	Vinyl acetate copolymer	3.25	17.87	3.5	3.6	3.0	-
National Starch 2211	Vinyl acetate copolymer	3.25	12.33	2.4	5.0	3.6	-
National Starch 2833	Vinyl Acrylic terpolymer	2.63	9.12	0.0	0.1	0.6	0.1

SEM MICROGRAPH OF "BORDEN 571" BOUND RANDOM MAT

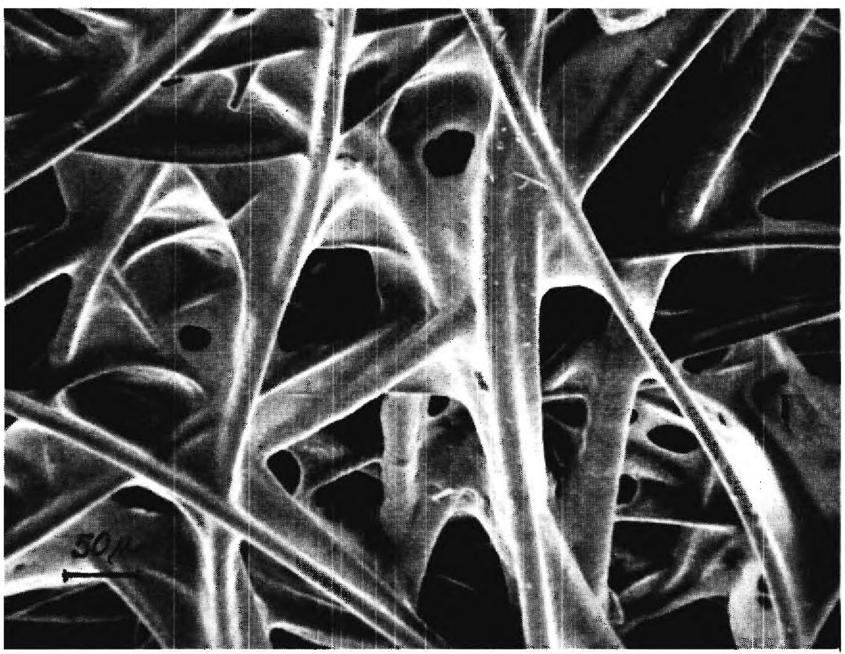


FIGURE 2.5.

systems when used for glass fiber products, is poor suggesting that other improved binders, e.g., that based on ethylene-acrylic acid copolymers as suggested by Dr. Eckstein of Union Carbide, would be needed.

2.3.2 Composites

A) Phenoxy Resin Composites

Table 2.4. summarizes the results of testing of the phenoxy-impregnated unaligned mats and aligned webs.

Because of general concern at Union Carbide and at Georgia Tech over the validity of the results of modulus measurements by the ultrasonic procedure, the measurements were repeated by Instron mechanical testing. While the results of both procedures do indicate that higher moduli (in the process axis direction) are achieved with the composites of aligned webs, as contrasted with those of unaligned mats, the degree of improvement obtained through use of aligned webs is more clearly illustrated by the Instron results.

Certain of the composites were produced from mats, aligned and unaligned, which were covered by carbon blocks during the carbonization process to eliminate fiber disorientation due to air currents in the ovens. The results obtained for the composites prepared from these protected mats are analyzed in Table 2.5. The composite moduli are given and are normalized to 50% volume/volume composites. Based on the composite properties, a modulus of elasticity in the direction of fiber alignment is found which is 2.5 times greater than that of the random mat indicating clearly that a substantial degree of alignment has been achieved. The "random/unidirectional (R/U)" ratio is 0.40 (see Table 2.1.).

The values for fiber volume which are reported are based on a weighing procedure used at Union Carbide. The values of moduli are low for a 30% CF-loaded composite. They

TABLE 2.4. Composite Strengths--Phenoxy Matrix

NO.	SAMPLE DESCRIPTION	V_f*	AVERAGE SONIC MODULUS		AVERAGE INSTRON MODULUS**		NORMALIZED (50% v/v) INSTRON MODULUS	
			psi X 10^{-6}	G Pa	psi X 10^{-6}	G Pa	psi X 10^{-6}	G Pa
1	Aligned, Carbonized	0.302	1.50	10	0.99	7	1.64	11.3
2	Aligned, Carbonized	0.364	0.71	5	1.36	9.5	1.87	12.9
3	Unaligned, Carbonized	0.275	1.30	9	0.79	5.5	1.38	9.5
4	Unaligned, Carbonized	0.294	1.18	8	0.74	5	1.26	8.7
5	Aligned, Carbonized, with Blocks	0.325	1.15	8	1.26	9	1.94	13.4
6	Aligned, Carbonized, with Blocks	0.301	1.74	12	1.57	11	2.61	18.0
7	Aligned, Carbonized with Blocks	0.270	1.61	11	1.25	8.5	2.32	16.0
8	Unaligned, Carbonized, with Blocks	0.284	0.79	5.5	0.485	3	0.85	5.9
9	Unaligned, Carbonized, with Blocks	0.282	0.96	6.5	0.54	4	0.96	6.6
10	Unaligned, Carbonized	0.323	0.81	5.5	0.38	2.5	0.58	4.0
11	Unaligned, Carbonized	0.310	1.15	8	0.94	6.5	1.51	10.4

*V_f - calculated from weight of resin and fiber used in composite fabrication (Union Carbide procedure).

** Minimum of Two Determinations.

TABLE 2.5. Composite Strengths--Phenoxy Resin With "Protected" Mats

SAMPLE DESCRIPTION	SAMPLE NO.	V_f	INSTRON COMPOSITE MODULUS psi X 10^{-6}	INSTRON COMPOSITE MODULUS G Pa	NORMALIZED (50% v/v) INSTRON COMPOSITE MODULUS psi X 10^{-6}	NORMALIZED (50% v/v) INSTRON COMPOSITE MODULUS G Pa
Aligned Web, Carbonized Between Carbon Blocks	5	0.325	1.26	8.7	1.94	13.4
	6	0.301	1.54	10.6	2.56	17.7
	7	0.270	1.25	8.6	2.32	16.0
	Average				2.27	15.7
Unaligned Mat, Carbonized Between Carbon Blocks	8	0.284	0.485		0.85	5.9
	9	0.282	0.543		0.96	6.6
	Average				0.91	6.2

$$\frac{E \text{ aligned}}{E \text{ unaligned}} = 2.50$$

fall in the range of values which have been achieved with the polyester composites produced at much lower loadings.

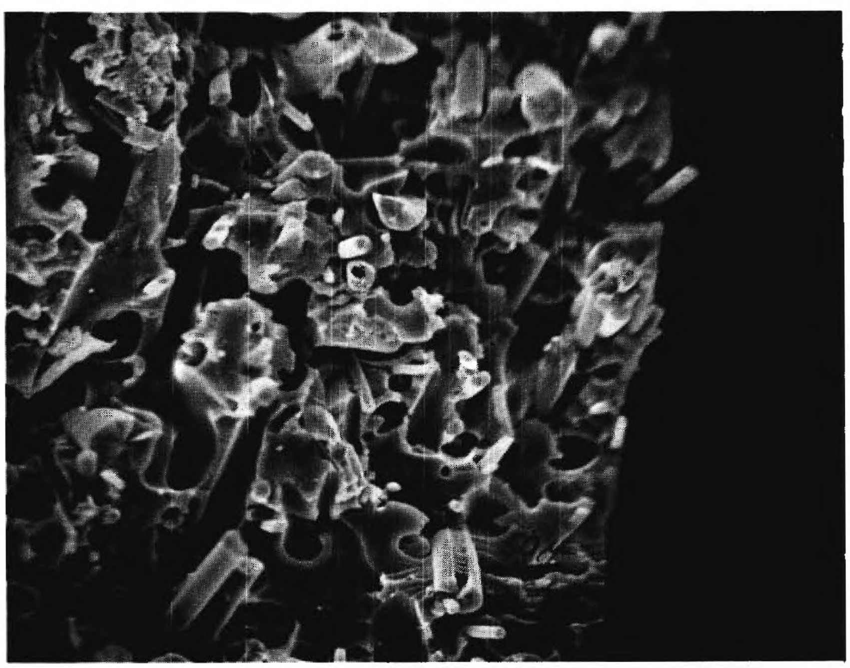
Studies by scanning electron microscopy of many of the phenoxy composites have demonstrated that large voids within and at the surface of the composites is experienced.

In Figure 2.6., the fracture surfaces for two composites of PHKC phenoxy, one with aligned web and the other produced from unaligned mat, are presented. The variability in degree of orientation of fibers can be seen to be much greater in the "unaligned" composite, as contrasted with the "aligned" composite. It is clear also that the principal mode of failure is due to inefficient bonding between the matrix and fiber, as evidenced by fiber pull-out. The photographs were taken at a magnification of 200X.

FIGURE 2.6.

COMPOSITE FRACTURE SURFACE PHKC - RESIN
PERPENDICULAR TO THE DIRECTION OF THE
PROCESS FLOW

UNALIGNED



ALIGNED

B) Epoxy

The serious difficulties with successful impregnation of the carbon mats was due to the discontinuous nature of the reinforcement and to the low viscosity of the epoxy at moulding temperature.

The objective in composite fabrication was to take advantage of fiber alignment in order to achieve high packing fraction at sufficiently low molding pressures to minimize fiber breakdown. However, insufficient molding pressure does not allow effective consolidation of the composite, leading to low fiber volume fractions and excessive void inclusions. Consequently, fabrication problems are critical to success. Because of the difficulties experienced with Epon 828, and because of the limited time available, it was decided to use a more controllable polyester system for fabrication on the assumption that the axial mechanical properties of the mat composites would be largely independent of the nature of the matrix. Additionally, it was thought possible to produce a well-consolidated polyester-carbon composite with respectable transverse properties.

C) Unsaturated Polyester

The results of mechanical testing for the composites produced using the polyester matrix are summarized in Table 2.6. The values of modulus have all been normalized to that of a composite containing 50% by volume of carbon fibers.

The objective of this phase of the project was to determine the degree of improvement of alignment achieved by the GT process vis-a-vis that of the random mat produced by Union Carbide.

TABLE 2.6. Composites Data--Polyester

Part A. Random Carbon Fiber Mat

Sample No.	Molding	MODULUS OF ELASTICITY psi	MODULUS OF ELASTICITY GN/m^2	FIBER VOLUME Acid	FIBER VOLUME Pyrolysis	MODULUS (NORMALIZED) TO 50% v/v psi X 10^{-6}	MODULUS (NORMALIZED) TO 50% v/v GN/m^2
3-1	Vac. Bag	516,000	3.5				
3-2		589,000	4.1		20.4	1.45	10
22-1	Vac. Bag	626,000	4.3	10.0		3.15	21.5
22-2		620,000	4.3		8.9	3.5	24
22, Avg.						3.3	22.9
23-1	Vac. Bag	459,000	3.2		16.2	1.4	9.5
23-2	Vac. Bag	423,000	2.9		15.3	1.4	9.5
23, Avg.							

$(10^6 psi) \times 6.896 = GN/m^2 \simeq GPa$

TABLE 2.6. (cont'd)

Part B. Aligned Carbon Fiber Mat

Sample No.	Molding	MODULUS OF ELASTICITY psi	MODULUS OF ELASTICITY GN/m^2	FIBER VOLUME Acid	FIBER VOLUME Pyrolysis	MODULUS (NORMALIZED) TO 50% v/v psi X 10^{-6}	MODULUS (NORMALIZED) TO 50% v/v GN/m^2
4-1	Vac. Bag	723,000	5.0	9.0		4.0	27.5
4-2	Vac. Bag	583,000	4.0	4.9		6.0	41.4
4, Avg.						5.0	34.4
5-1	Vac. Bag	425,000	2.9		10.3	2.05	14
5-2	Vac. Bag	862,000	5.9		10.0	4.3	29.5
5-3	Vac. Bag	794,000	5.5		5.3	7.5	51.5
5, Avg.	Vac. Bag					4.6	31.7
6-1	Vac. Bag	739,000	5.1		9.1	3.75	25.9
6-2		900,000	6.2		11.2	4.0	27.5
6, Avg.						3.9	26.7
7-1		1,520,000	10.5		11.4	6.65	46
7-2		1,440,000	9.9		8.4	8.55	58.5
7, Avg.						7.60	52.3
11-2	Vac. Bag	811,000	5.6		12.3	3.3	22.8

TABLE 2.6. (cont'd)

Part B. (cont'd)

Sample No.	Molding	MODULUS OF ELASTICITY		FIBER VOLUME		MODULUS (NORMALIZED) TO 50% v/v	
		psi	GN/m^2	Acid	Pyrolysis	psi X 10^{-6}	GN/m^2
12-1	Vac. Bag	1,240,000	8.6		19.7	3.15	21.5
12-2	Vac. Bag	1,550,000	10.7		22.3	3.5	24
12, Avg.						3.33	23
15-1	Vac. Bag	1,010,000	7.0	23.6		2.15	15
15-2	Vac. Bag	1,230,000	8.5	17.4		3.55	24.5
15, Avg.						2.85	19.8
16-1	Vac. Bag	805,000	5.6	11.8		3.4	23.5
16-2	Vac. Bag	868,000	6.0	14.1		3.1	21.5
16, Avg.						3.25	22.4
17-1	Vac. Bag	789,000	5.4		12.4	3.2	22.1
17-2	Vac. Bag	704,000	4.9		10.9	3.25	22.4
17, Avg.						3.23	22.2
18-1	Vac. Bag	799,000	5.5		12.3	3.25	22
18-2	Vac. Bag	710,000	4.9		12.6	2.8	19
18, Avg.						3.0	20.7

TABLE 2.6. (cont'd)

Part B. (cont'd)

Sample No.	Molding	MODULUS OF ELASTICITY psi	MODULUS OF ELASTICITY GN/m^2	FIBER VOLUME Acid	FIBER VOLUME Pyrolysis	MODULUS (NORMALIZED) TO 50% v/v psi X 10^{-6}	MODULUS (NORMALIZED) TO 50% v/v GN/m^2
19-1	Lay-up	565,000	3.9		12.1	2.35	16
19-2	Lay-up	563,000	3.9	10.6		2.65	18
19, Avg.						2.5	17.2
20-1	Lay-up	657,000	4.5	8.6		3.8	26
20-2	Lay-up	622,000	4.3		9.3	3.35	23
20, Avg.						3.58	24.7

The index for alignment is based on the ratio of the modulus of the composite of the aligned web (in the machine direction) to that of the modulus of composites produced from "random mat". Unlike the phenoxy composites, the "aligned" webs used in this study were produced from alignment of carbonized, random mat directly.

An examination of the results for the normalized modulus of elasticity for the "random" or "unaligned" composites (Part A, Table 2.6.) shows that a range of from 1.4 to 3.5 X 10^6 psi (9.5 to 24 GPa) is measurable, with an average value being 2.05 X 10^{-6} psi (14 GPa).

The normalized data for the composites produced from aligned carbon fiber mat produces a range of moduli from 2.1 to 8.6 X 10^6 psi (14 - 59 GPa) with an average value of 3.9 X 10^6 psi (27 GPa).

It must be recognized that this is normalized data and that there is substantial scatter in the data. The data for sample number 5 (i.e., 5-1, 5-2, and 5-3) which has the most scatter is due to poor resin setting properties during fabrication which resulted in erratic flow properties. Except for that particular sample, however, there was no obvious problem with fabrication of the remaining reported samples. Nevertheless, caution is recommended in deriving conclusion based on this data. Therefore, it is useful to regard the apparent ratio of 1.9 (average "aligned" moduli-to-average "random" moduli) as an approximate index of the degree of preferential alignment.

Based on our earlier derivation (equation 2.15), the moduli of composites produced from randomly aligned mats in a laminar construction, at fiber volume fractions of 15% and moduli of elasticity of 450,000 psi and 25,000,000 psi, for the resin and fibers, should be:

$$E_{c_r}^{15\%} = 1.55 \times 10^6 \text{ psi} \qquad \text{(random)}$$

The corresponding value for unidirectionally-oriented webs in a laminar construction is:

$$E_{c_u}^{15\%} = 4.13 \times 10^6 \text{ psi}$$

On a 50% fiber volume basis, i.e., normalizing these results to correspond to the values of Table 2.6., one calculates the following values:

$$E_{c_r}^{50\%} = 5.2 \times 10^6 \text{ psi} \qquad \text{(for random mats)}$$

$$E_{c_u}^{50\%} = 13.8 \times 10^6 \text{ psi} \qquad \text{(for unidirectional webs)}$$

These values are derived for the ideal case where no void volume is encountered and, as such, represent the upper limits that one could expect to achieve with this study. They are presented here for general comparison purposes only, for use in the examination of the data of Table 2.6. Not unexpectedly, the values which are reported in Table 2.6. are considerably lower than those predicted on the basis of an ideal system. Not only are voids incorporated in the composites, but perfect alignment in the two-dimensional plane of a web is not achievable. Moreover, because of the presence of drafting waves, the assumption of perfect alignment of webs in the third dimension, i.e., perpendicular to laminar planes, is not valid. In addition, migration of discontinuous fibers in the resin matrix is unavoidable during fabrication, as is fiber breakage and poor packing efficiency.

The mechanical properties of the composites which were produced from the polyesters are of the same order of magnitude of those achieved with the phenoxy resin, despite the fact of low fiber volume loadings. A check of three different samples of the phenoxy-carbon composites by the pyrolysis method for fiber determination resulted in measurements of 17.9%, 16.0%, and 27.4% fiber volume fractions which differ significantly from the values reported using the "weighing" procedure.

As shown in Figure 2.7., further evidence of alignment of the fibers in the aligned web is provided by the photograph at 200X of the fracture surface of a polyester composite fabricated from aligned webs. Clumping ("drafting wave") and voids are apparent, in addition to aligned fibers which demonstrate preferred orientation.

FIGURE 2.7

COMPOSITE FRACTURE SURFACE: POLYESTER-ALIGNED CARBON COMPOSITE PERPENDICULAR TO DIRECTION OF PROCESS FLOW

CHAPTER 3. CONCLUSIONS AND RECOMMENDATIONS

This chapter is concerned with the development of conclusions based on the results of this research and development program, and expresses recommendations for developing improved and optimized process schemes.

3.1 FIBER HANDLING

The data presented in Chapter 1 clearly indicate that both pre-oxidized and carbonized pitch-based fiber can be handled with minimal fiber damage. However, attempts to align and attenuate the mat were hindered by the occurrence of drafting waves. These drafting waves decrease the uniformity of the aligned material and it is likely that they have a detrimental effect on composite modulus. Accordingly, it is recommended that Union Carbide pursue a program to significantly increase the uniformity of fiber length distribution of mat fiber to increase the efficiency of alignment and attenuation.

Over the duration of this project, it has become apparent that continuous filament pitch yarn will become more cost effective in subsequent years. Accordingly, it is suggested that staple fiber not be considered for manufacture into yarn. However, this research has pointed to the feasibility of making non-woven aligned fibrous assemblies from the mat. This finding should be definitely capitalized on, for it is expected that the performance/cost ratio of aligned mat could be made as high or possibly higher than that for continuous fiber. And this could open new markets for the material.

Further, it is recommended that the developments for fiber handling be studied carefully to see where they might be implemented in continuous filament operations to increase the efficiency of those operations. For example, the use of soft nip rollers has been employed effectively by Dr. Franz Nassem of the Parma Technical Center in a research project. The implementation of these developments in certain applications at Greenville might reduce the degree of end breakage during processing.

3.2 COMPOSITE FABRICATION

Webs of aligned, discontinuous carbon fibers are of little commercial significance unless they are capable of reinforcing low-modulus matrices effectively. In order to achieve effective reinforcement, the following requirements must be met in a composite:

(1) High fiber volume fraction

(2) Good packing efficiency

(3) Preferential orientation (with ability to vary direction of lay-up to meet design criteria)

(4) Low void content

(5) Efficient stress transfer between fibers (good adhesion, even fiber distribution)

(6) Narrow L/d distribution and critical length

The achievement of these properties is greatly hindered by the lack of uniformity among fibers in the starting material;

the variable nature of fiber structure, length distribution, diameter distribution, etc. It is possible that the introduction of a "grading" operation (e.g., hydrocycloning) could enhance the results achievable by the alignment and attenuation process which, in turn, would more closely match the requirements for a successful composite. There is also considerable scope for improvement of the alignment and attenuation process.

Commercial acceptance of a well-aligned web will depend on its ability to be fabricated into useful composites.

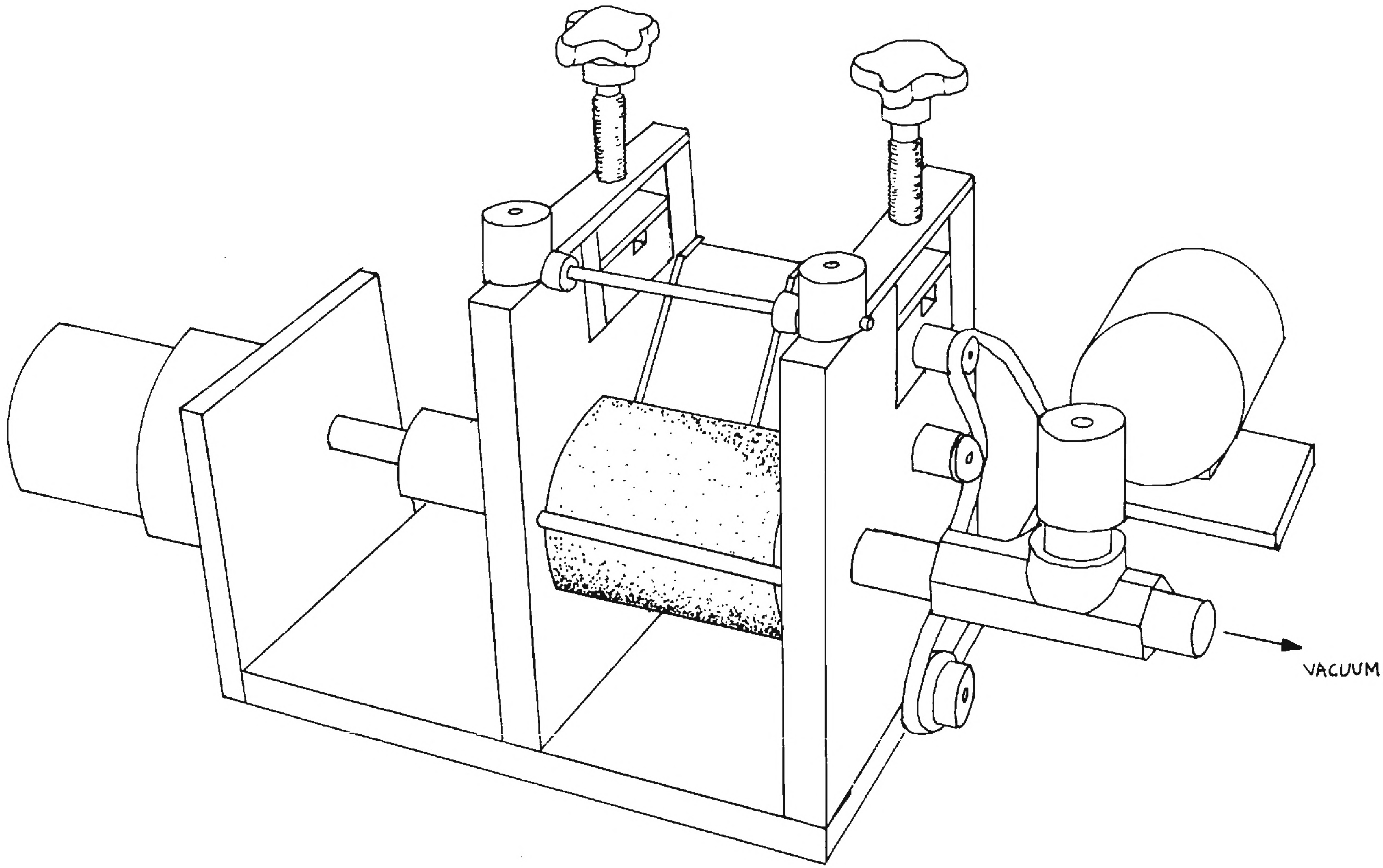
It is suggested, for future investigations and applications, that the web be lightly bonded with an adhesive system that will impart sufficient strength to allow easy handling and conformation to a mold, that the adhesive(s) be soluble in the resin system(s) to be used as a matrix, and that the adhesive reduces migration and prevents interfiber abrasion and fiber degradation during processing.

Resin systems must provide sufficient fiber-matrix bonding to allow for effective translation of the mechanical properties of the fibers. With higher volume fractions of fibers and fewer voids, it is believed that epoxy and polyester matrices will be suitable.

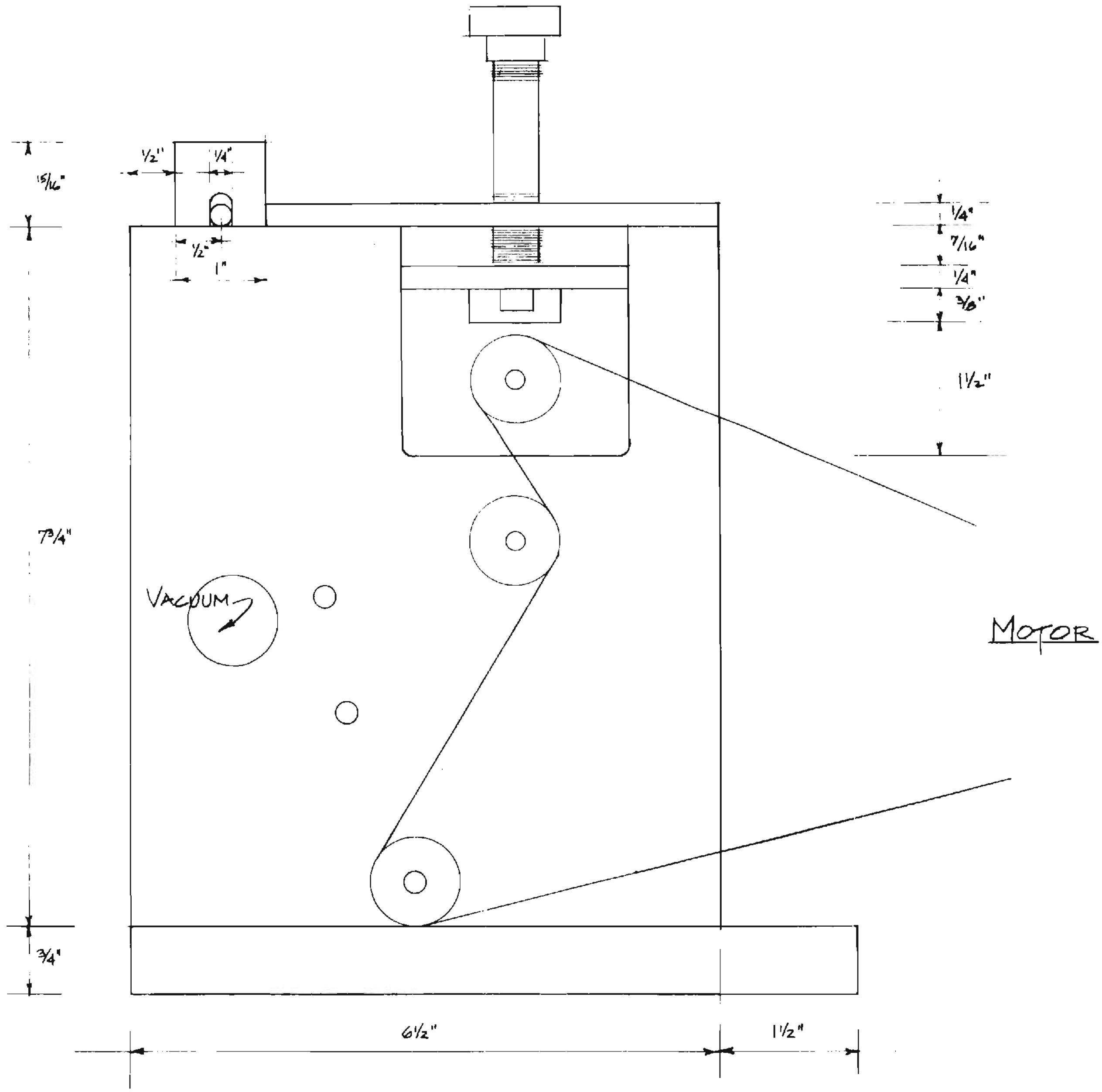
Finally, it is recognized that widespread application of a unidirectional carbon web will be dependent on economic factors. The existence of a market outlet for this product at a high volume level is probably critical. Since it appears that such a market will require a low-cost material, and since the raw material cost is volume-insensitive, it is essential that processing costs be kept to a minimum. It does appear, therefore, that future development of the alignment and attenuation process, with or without grading, should focus on process optimization both in an economic and technical context.

Appendix A

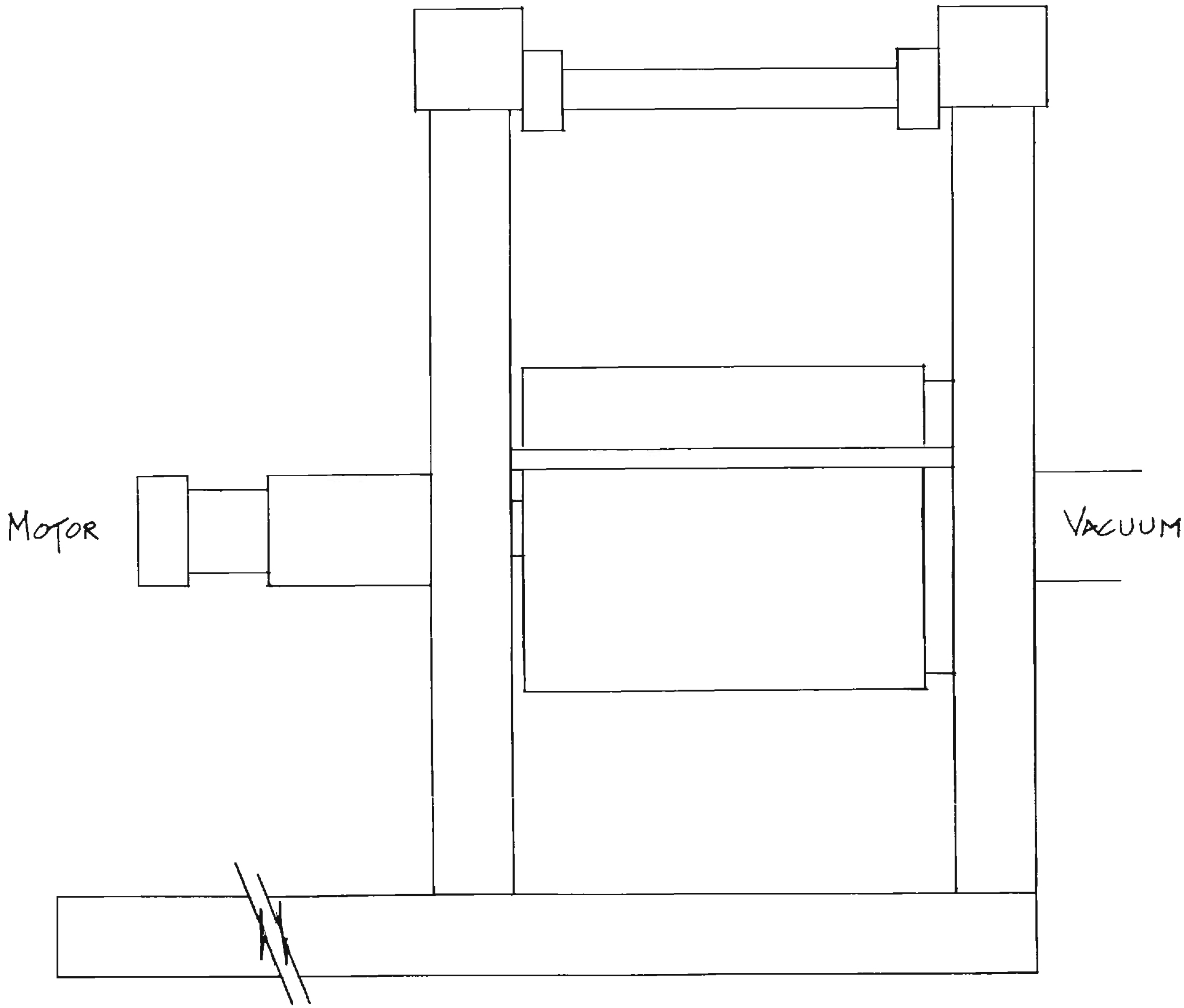
Engineering Drawings

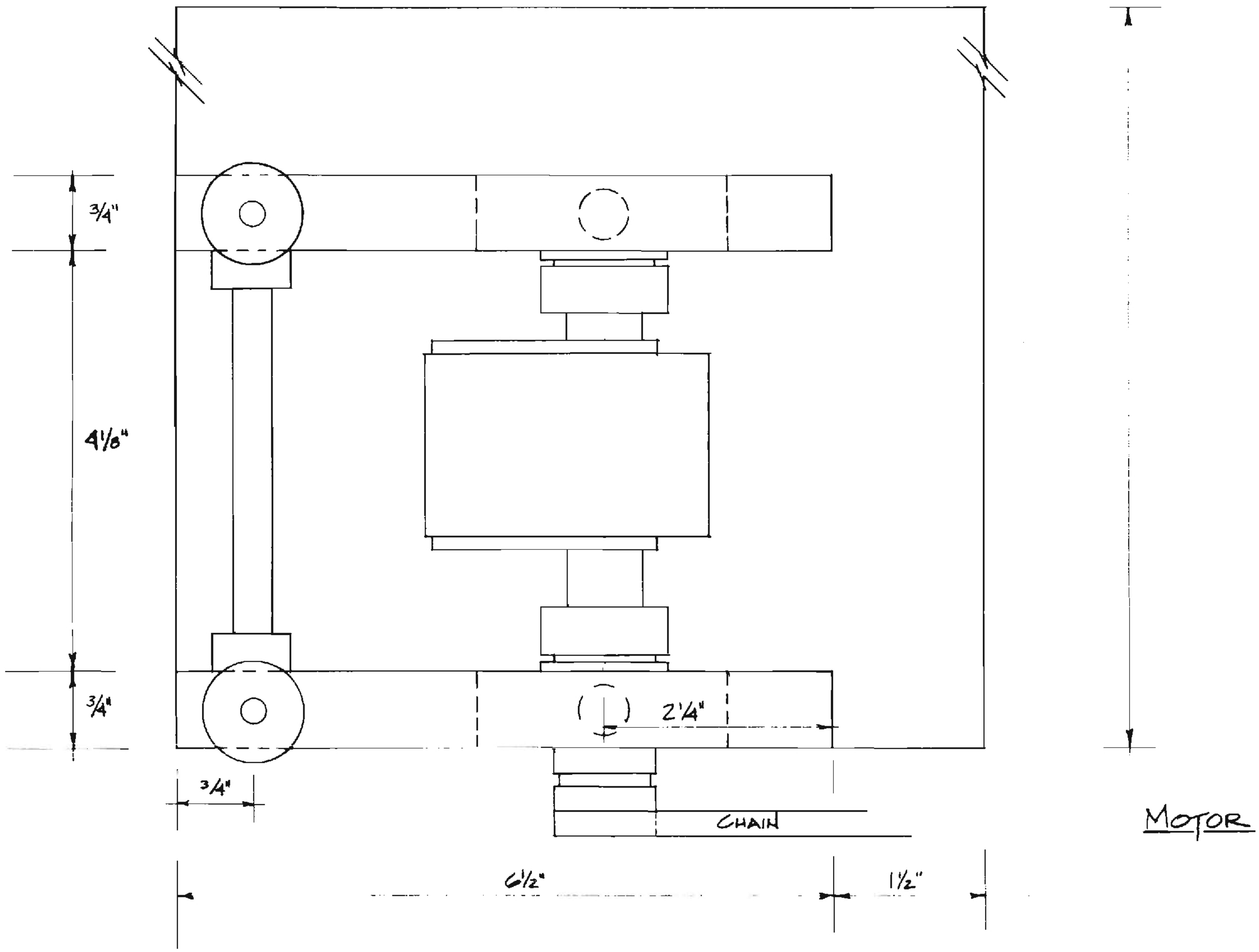


ALIGNMENT AND ATTENUATION DEVICE

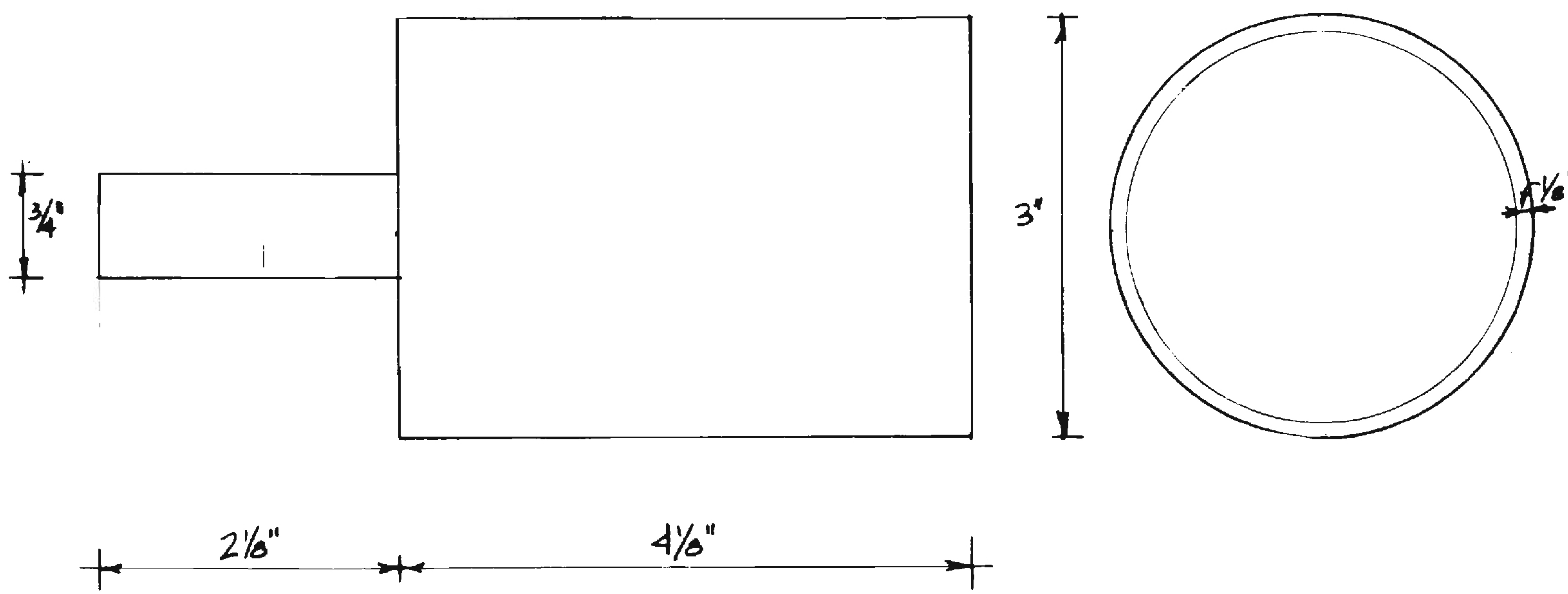


15/16"
1/2"
1/4"
1/2"
1"
1/4"
7/16"
1/4"
3/8"
1 1/2"
7 3/4"
VACUUM
MOTOR
3/4"
6 1/2"
1 1/2"

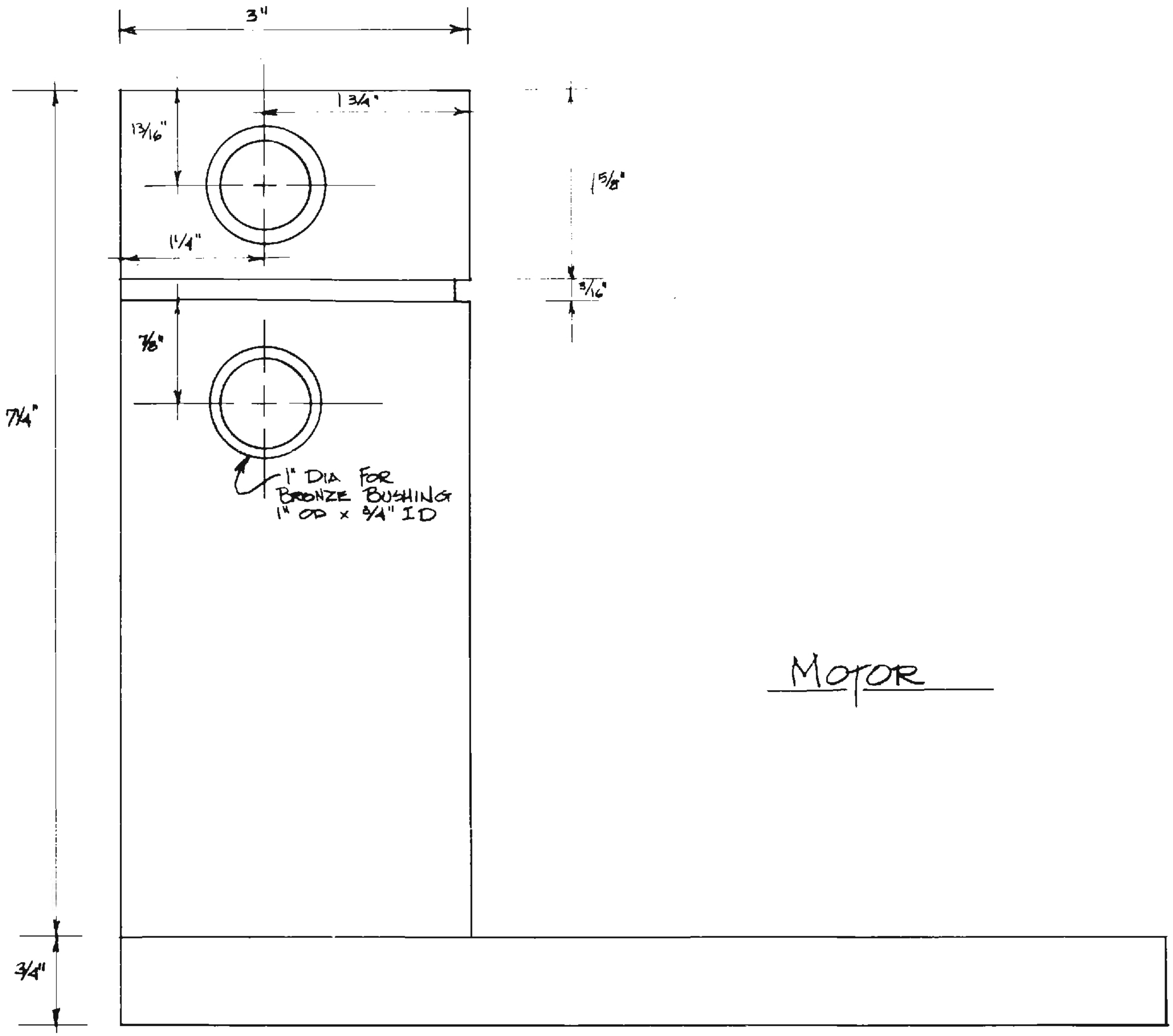

MOTOR
VACUUM



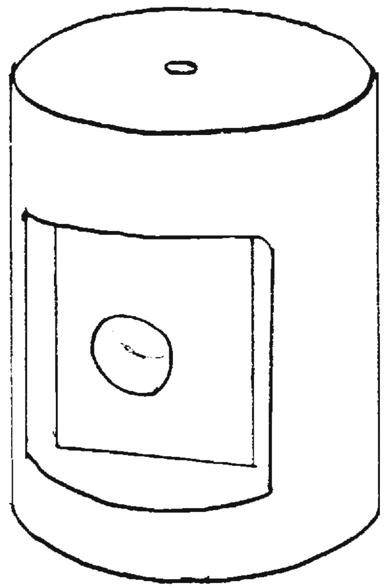
PINCH ROLLER



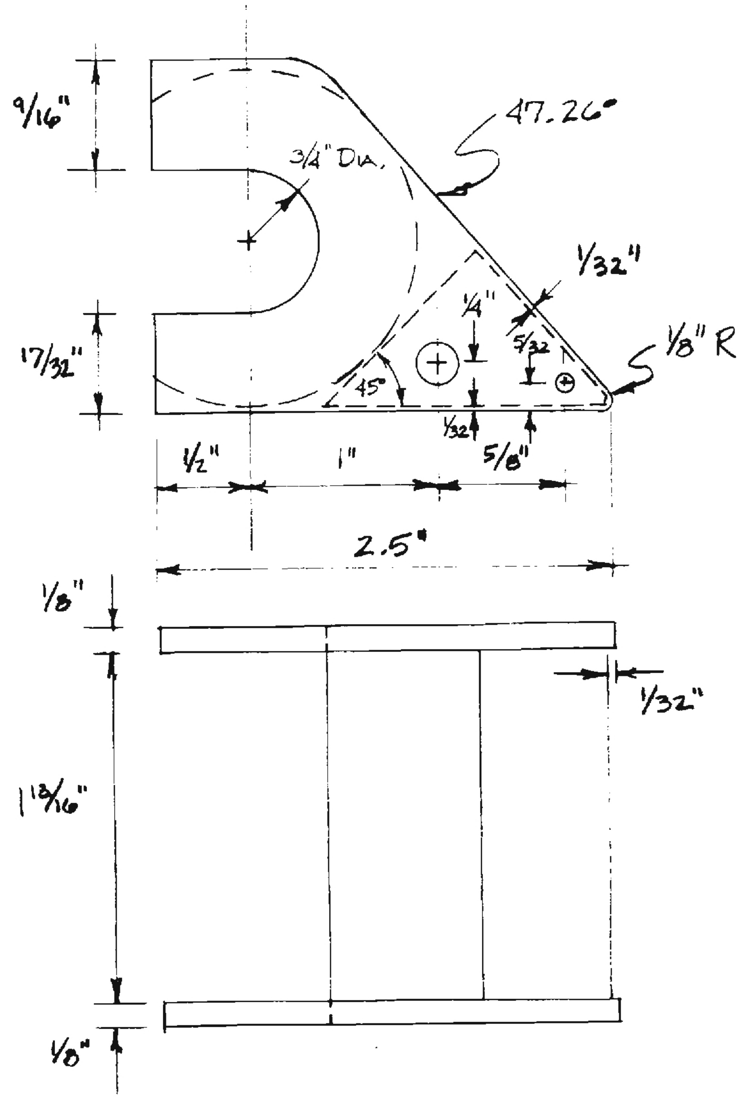
VACUUM ROLLER



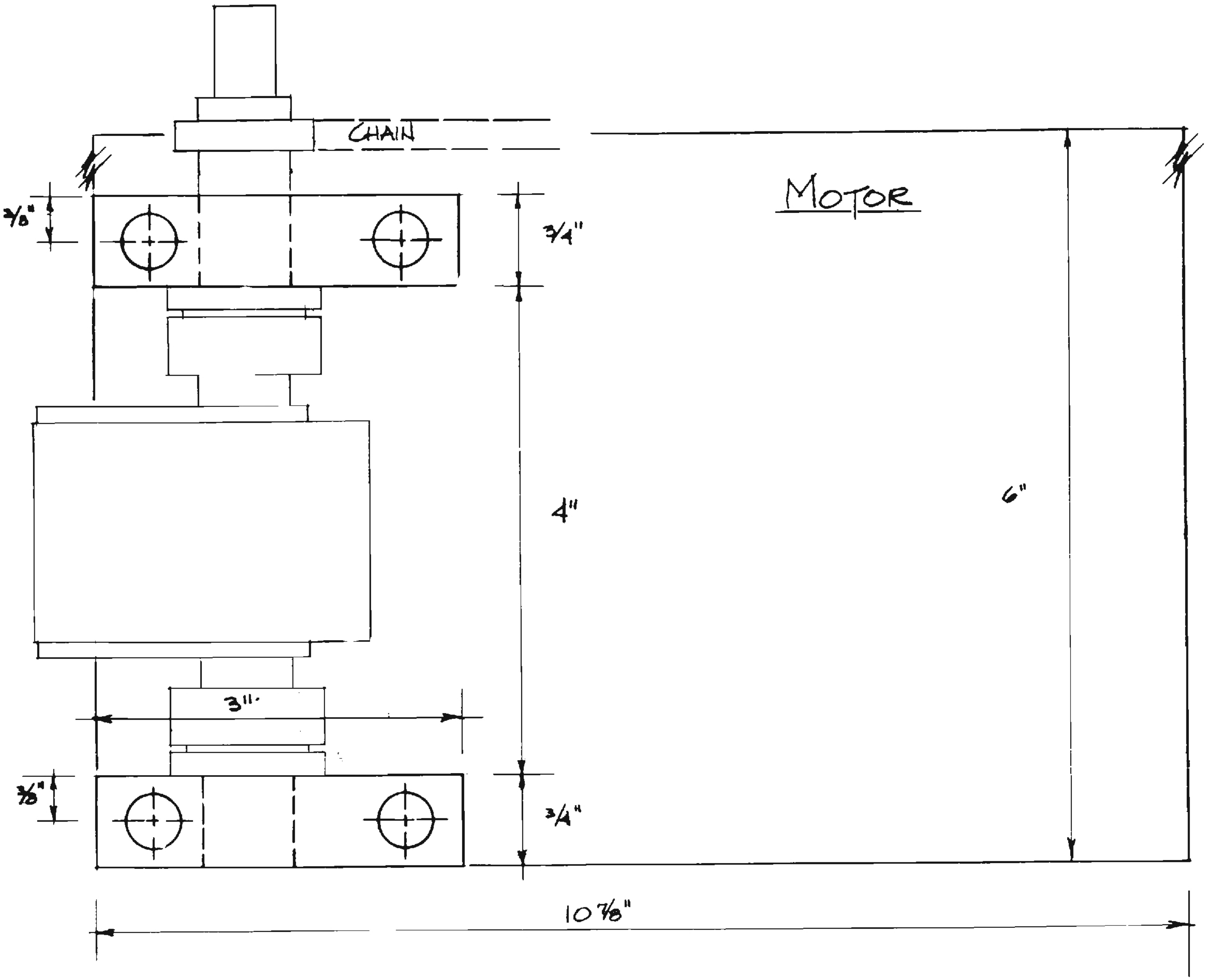
3"
1 3/4"
13/16"
1 5/8"
1 1/4"
3/16"
7/8"
7 1/4"
1" DIA FOR BRONZE BUSHING 1" OD x 3/4" ID
MOTOR
3/4"

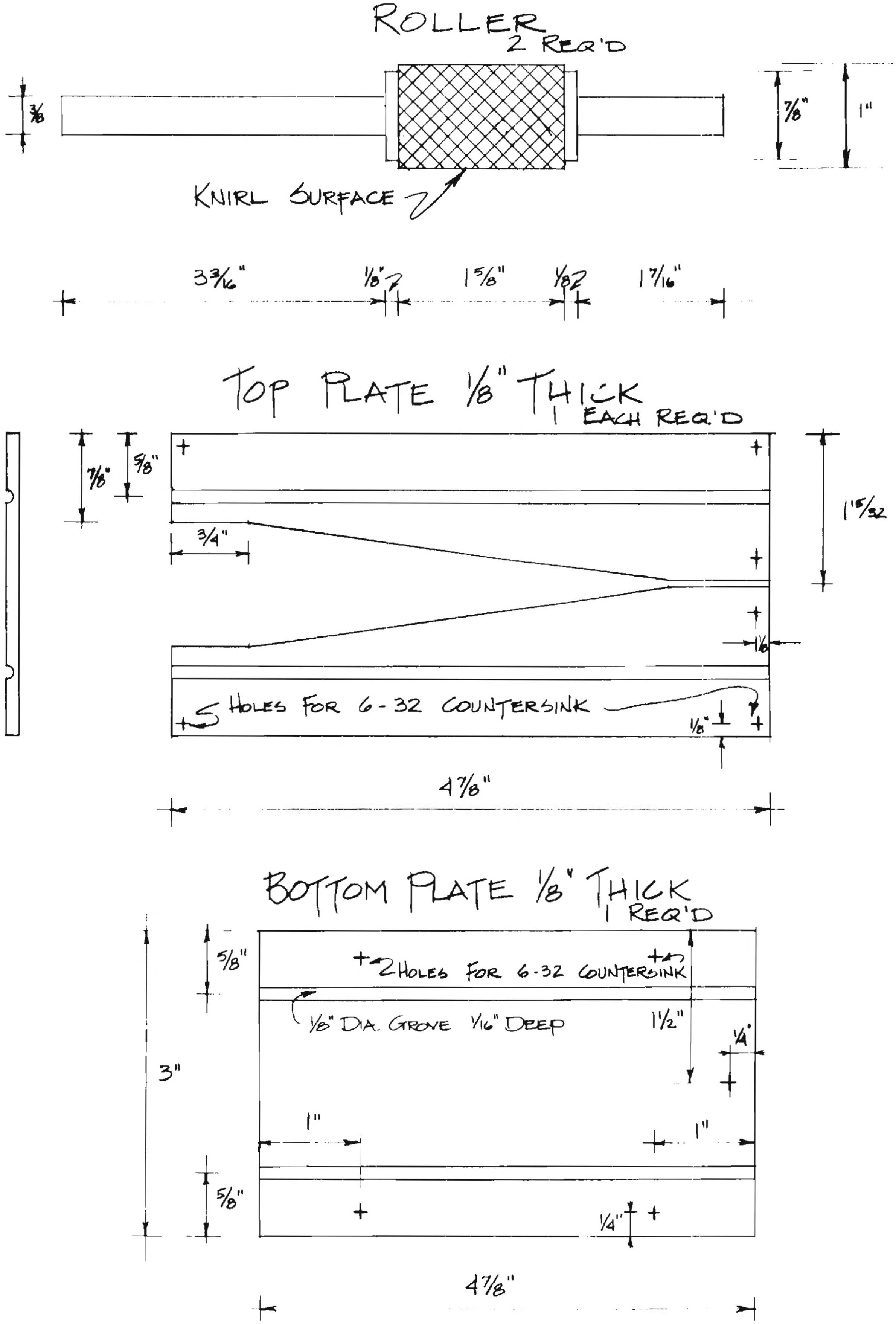


TEFLON BUSHING



APRON MOUNT


CHAIN
MOTOR
3/8"
3/4"
4"
6"
3"
3/8"
3/4"
10 7/8"



CONSOLIDATION DEVICE

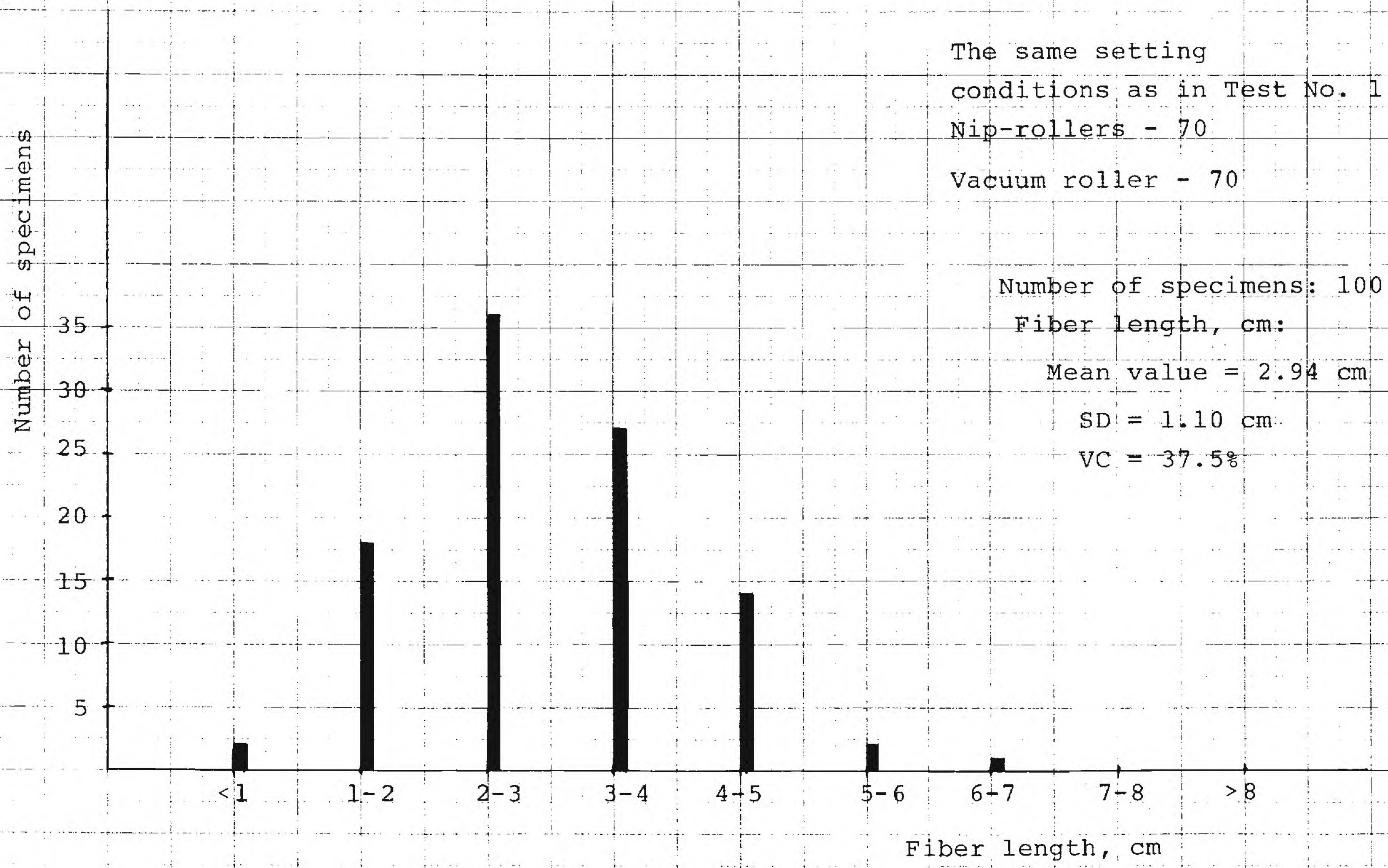
Appendix B

Fiber Length Distributions

Type 6

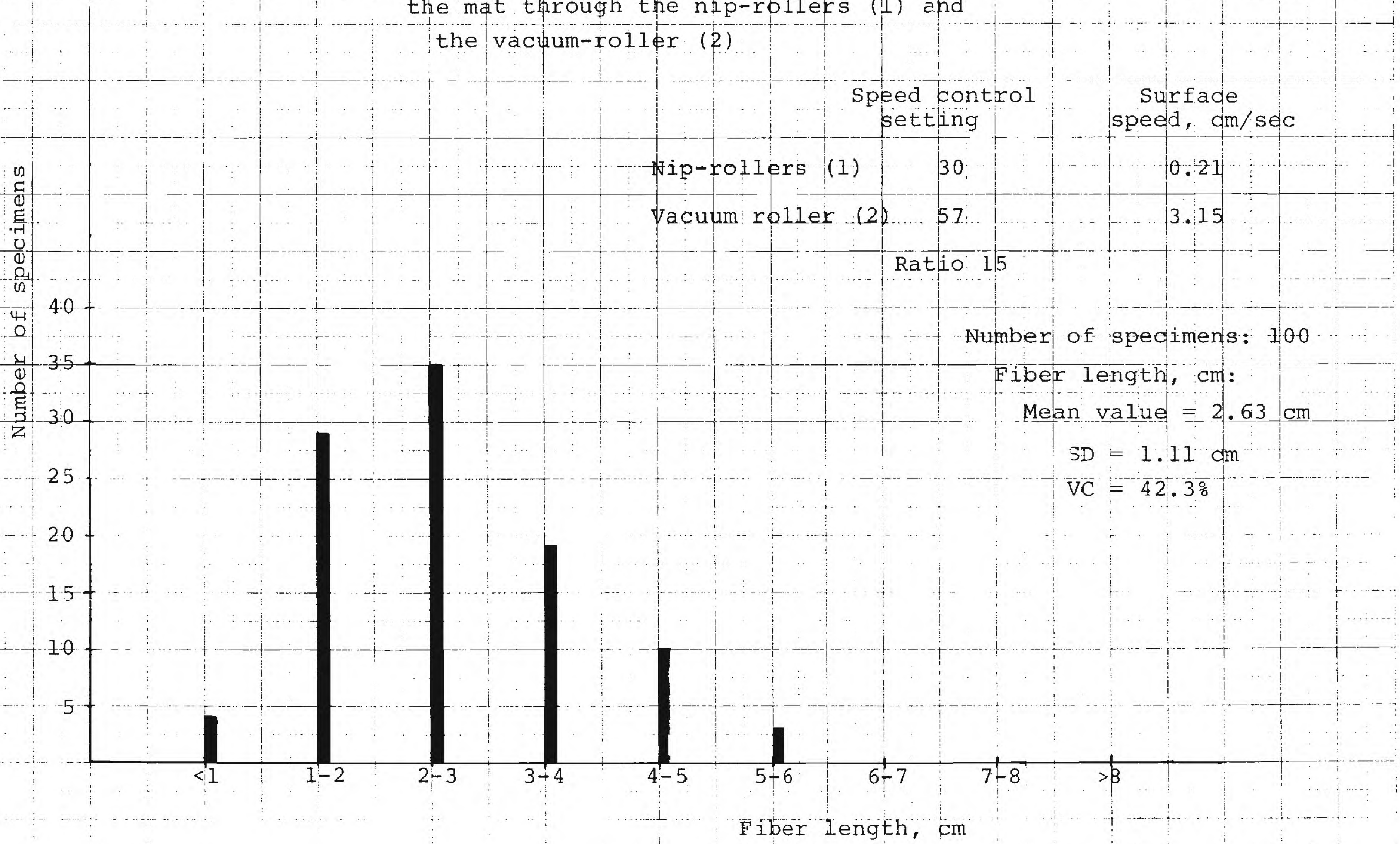
Test No. 2

Fiber length distribution in the web, after processing the mat through the nip-rollers (1) and the vacuum roller (2).



Type 6

Fiber length distribution in the web, after processing the mat through the nip-rollers (1) and the vacuum-roller (2)



Type 6

Fiber length distribution in the web, after processing the mat through the nip-rollers (1) and the vacuum roller (2)

	Speed control setting	Surface speed, cm/sec
Nip-rollers (1)	30	0.21
Vacuum roller (2)	72.5	4.2

Ratio 20

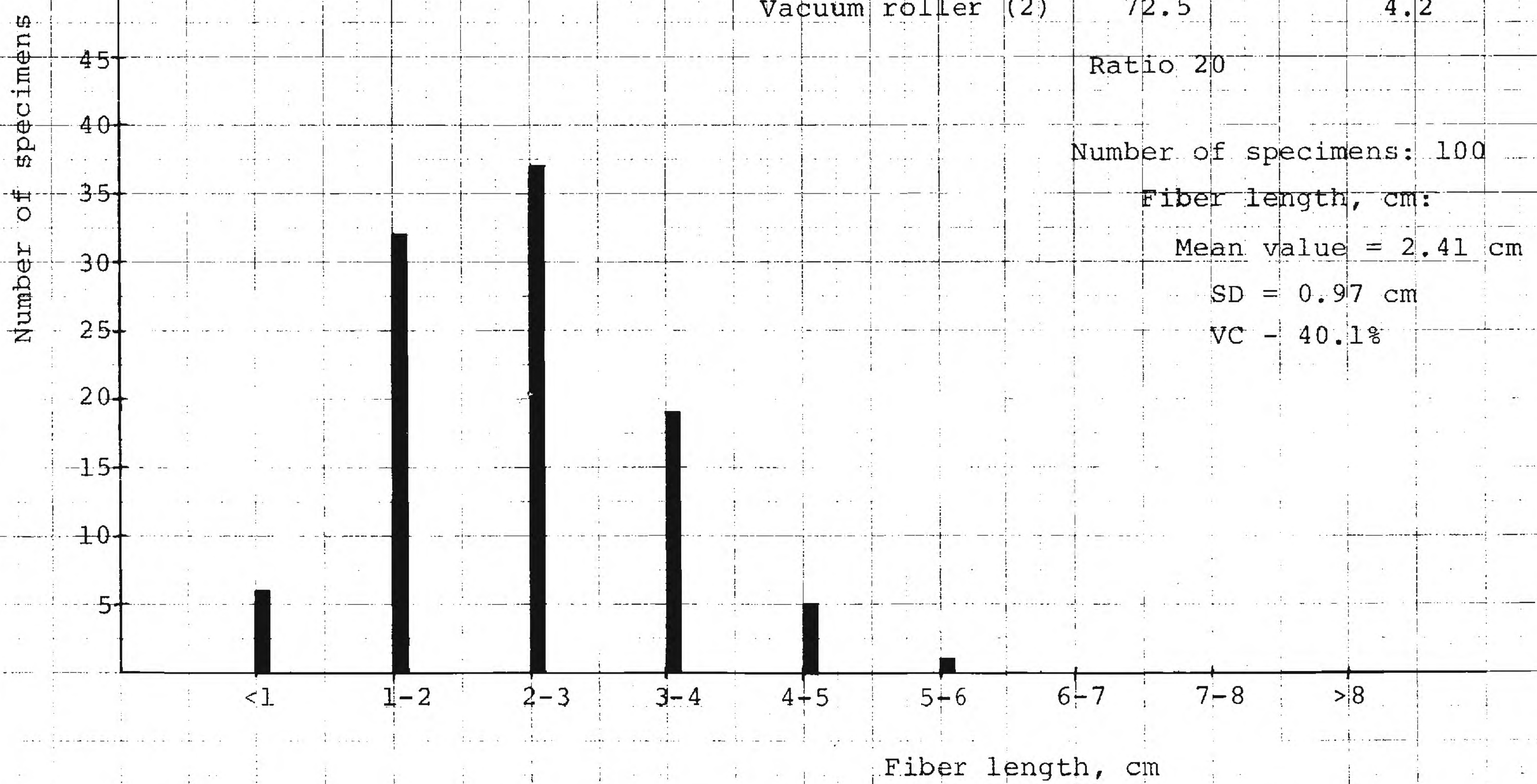
Number of specimens: 100

Fiber length, cm:

Mean value = 2.41 cm

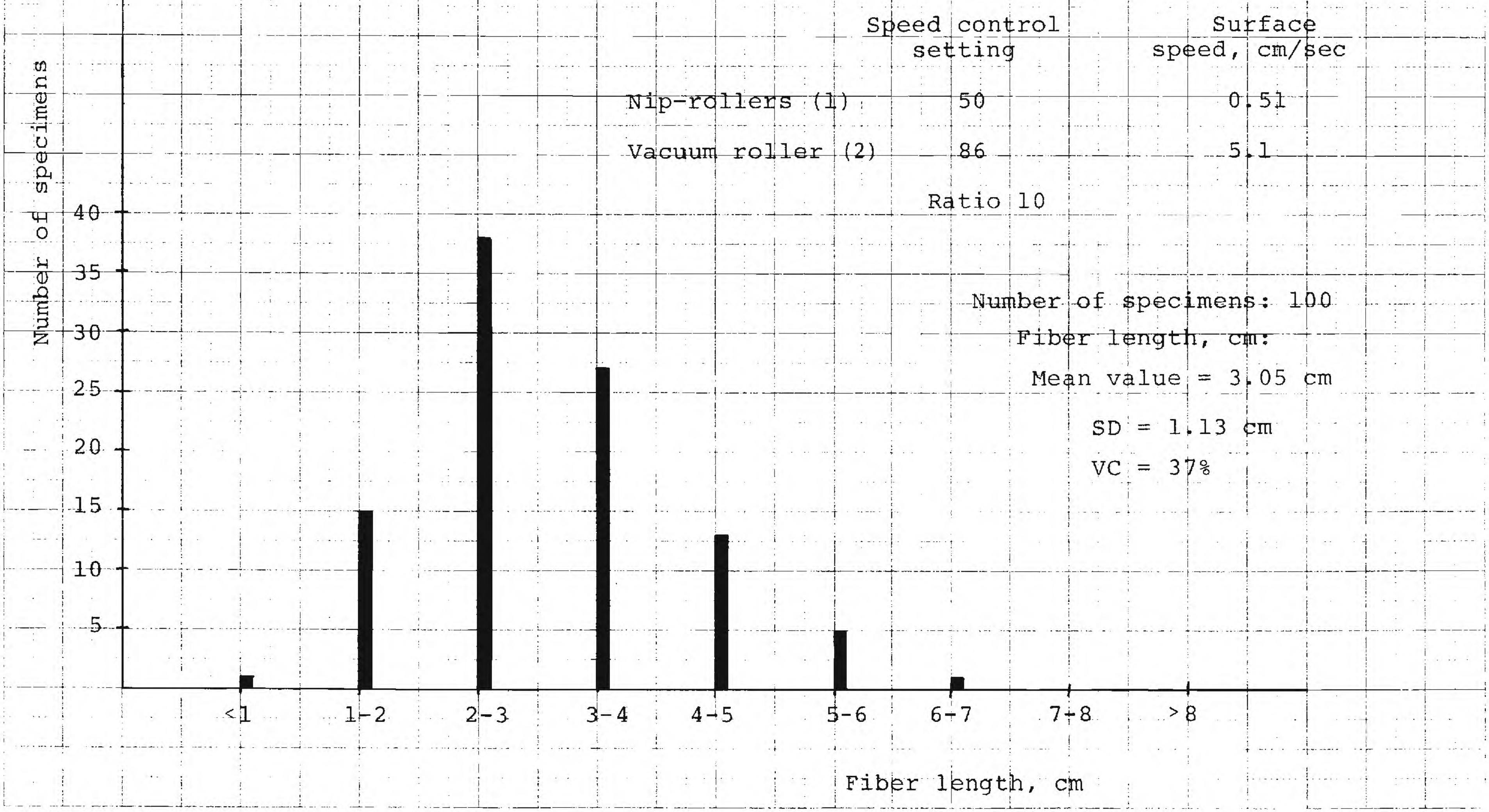
SD = 0.97 cm

VC - 40.1%



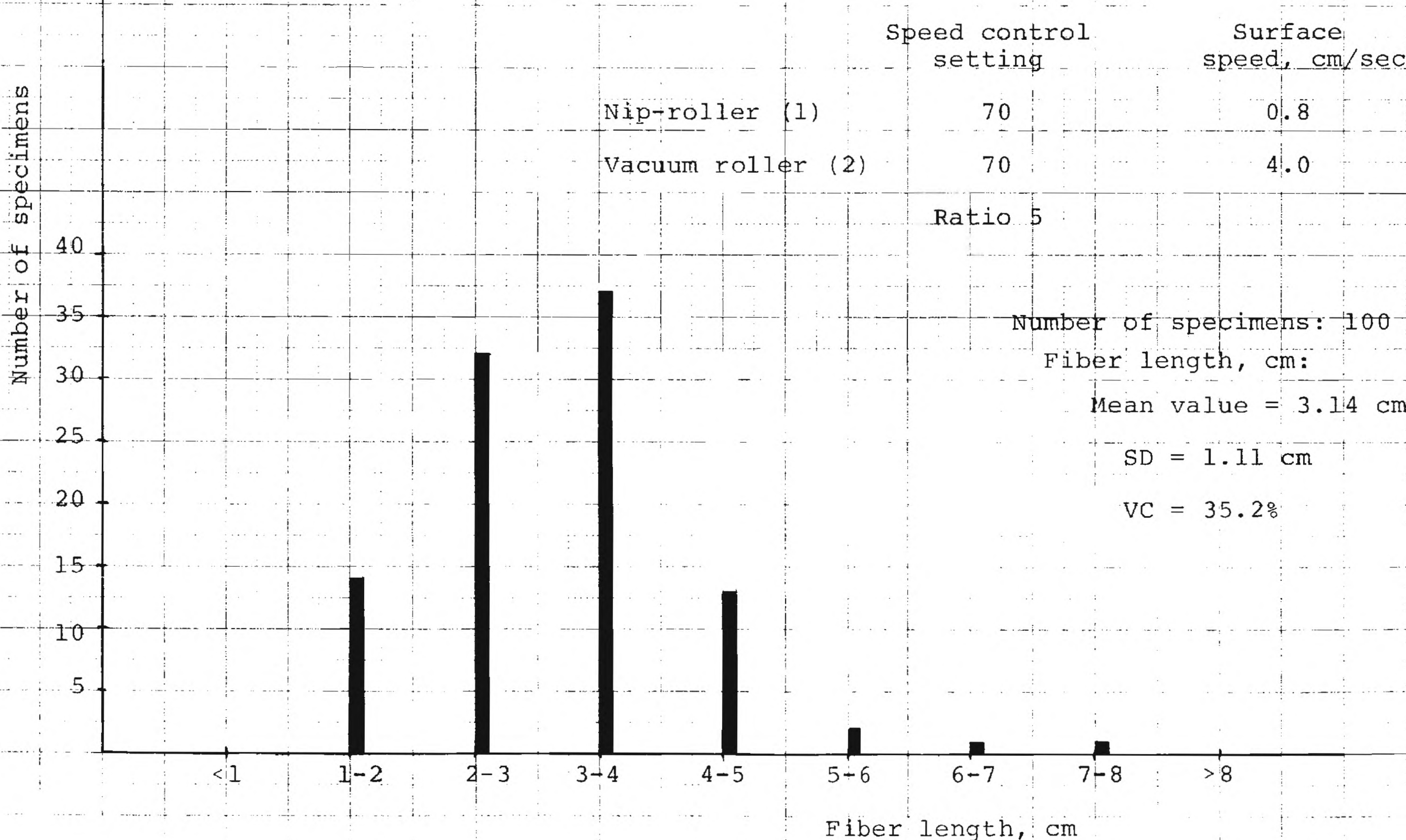
Type 6

Fiber length distribution in the web, after processing the mat through the nip-rollers (1) and the vacuum roller (2)



Type 6

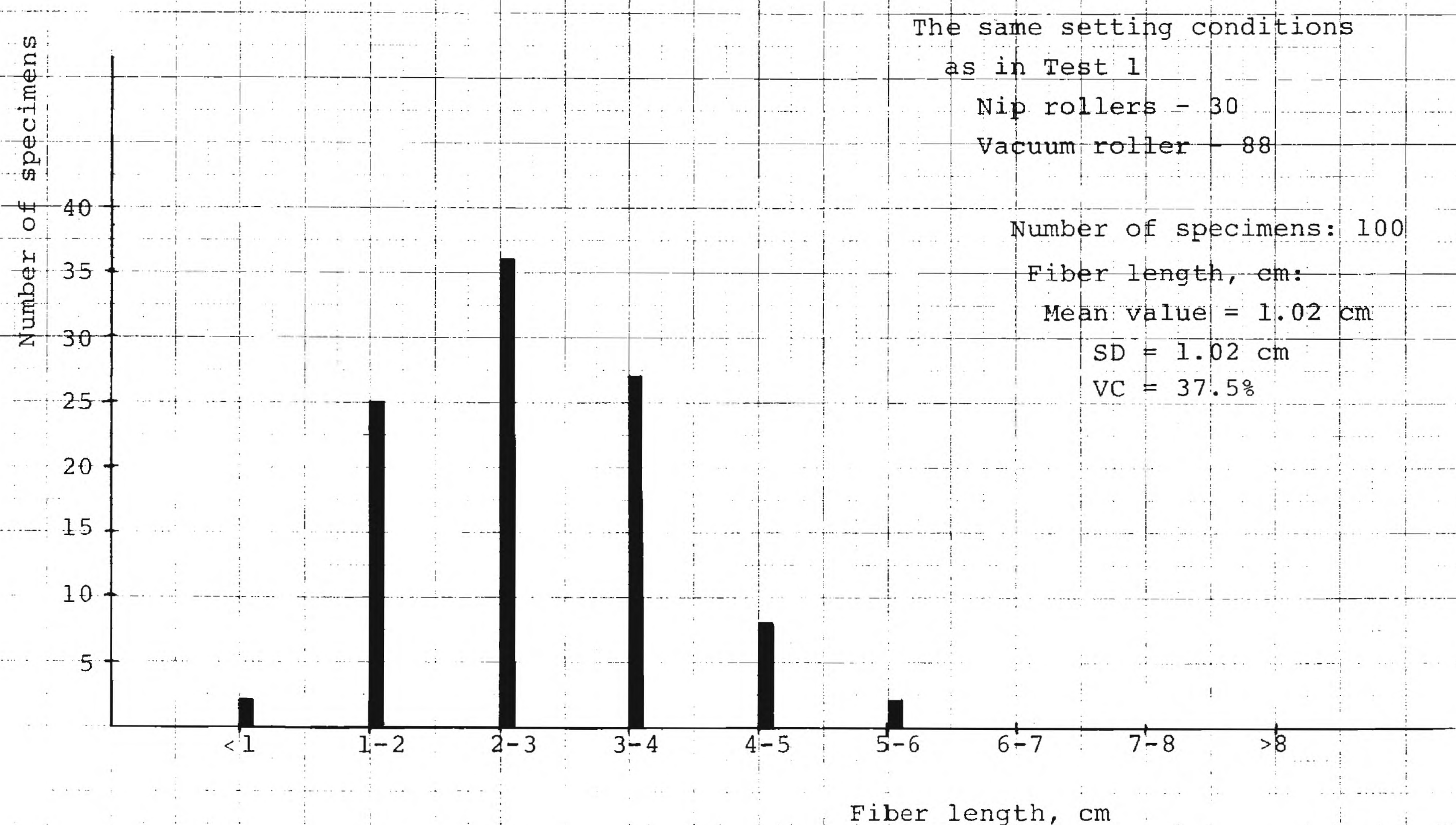
Fiber length distribution in the web, after processing the mat through the nip-rollers (1) and the vacuum roller (2)



Type 6

Test No. 2

Fiber length distribution in the web, after processing the mat through the nip-rollers (1) and the vacuum roller (2)



Type 6

Fiber length distribution in the web, after processing the mat through the nip-rollers (1) and the vacuum roller (2)

	Speed control setting	Surface speed, cm/sec
Nip-rollers (1)	30	0.21
Vacuum roller (2)	88	5.25
	Ratio 25	

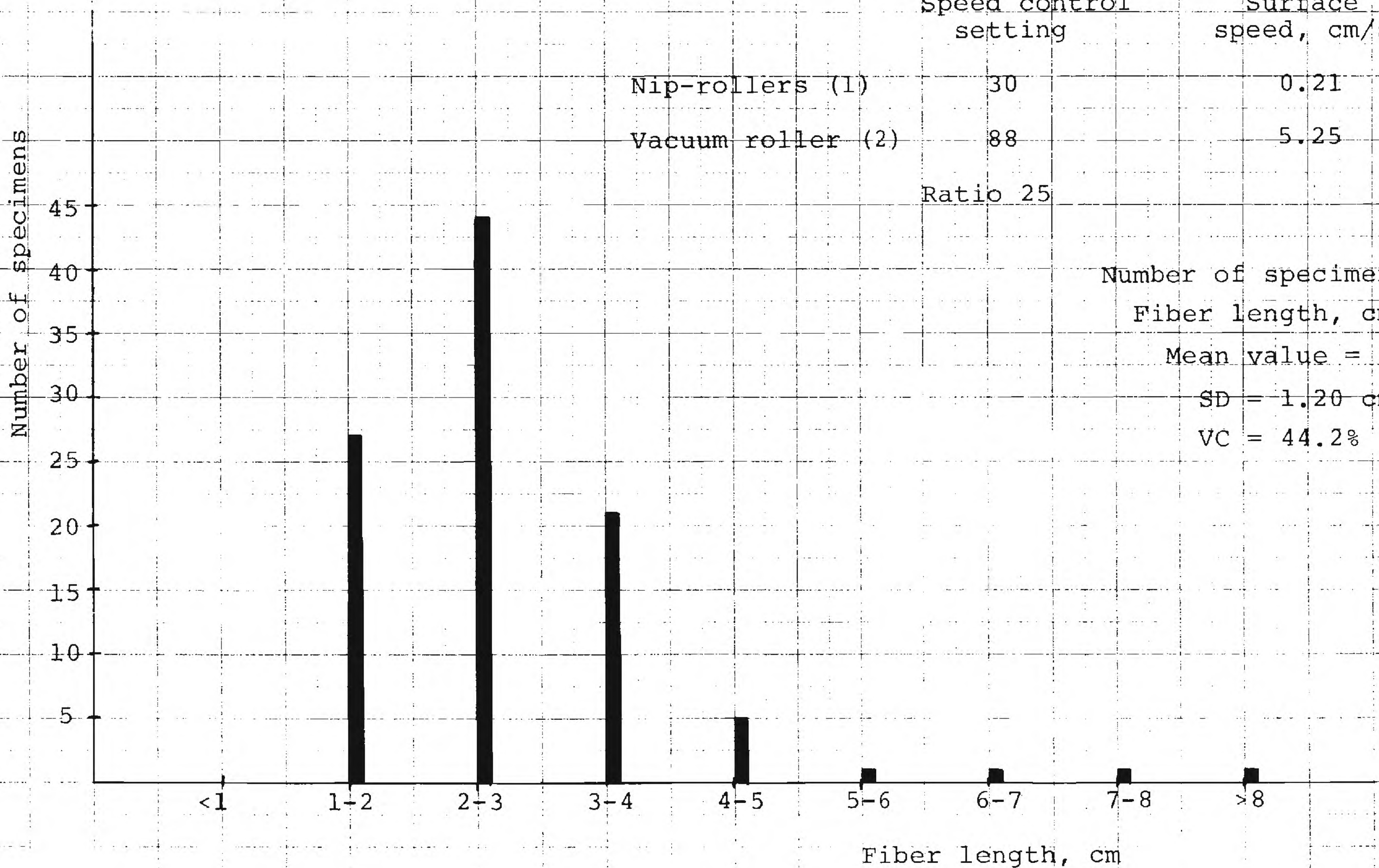
Number of specimens: 101

Fiber length, cm:

Mean value = 2.71 cm

SD = 1.20 cm

VC = 44.2%

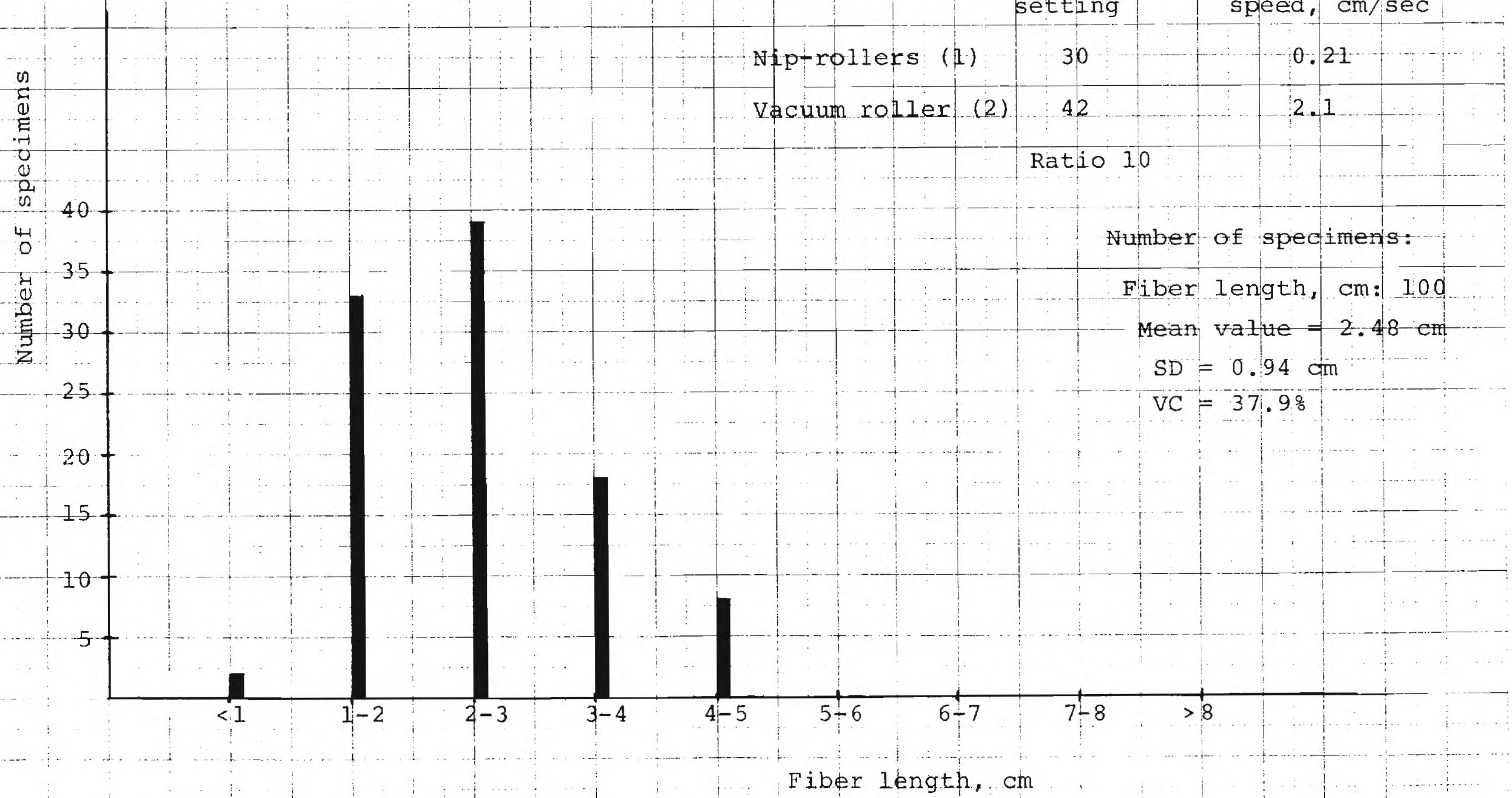


Type 6

Fiber length distribution in the web, after processing the mat through the nip-rollers (1) and the vacuum roller (2)

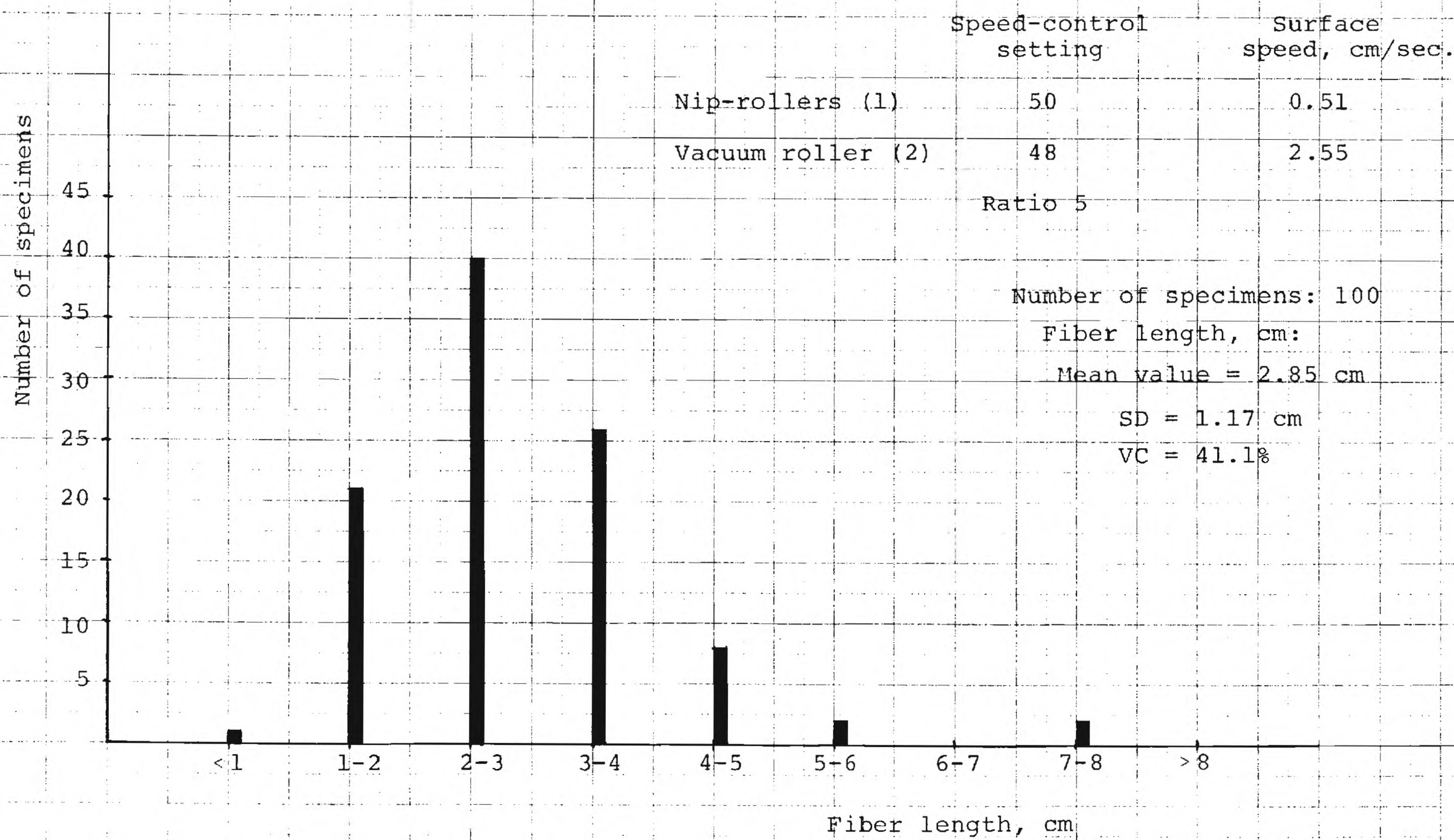
	Speed-control setting	Surface speed, cm/sec
Nip-rollers (1)	30	0.21
Vacuum roller (2)	42	2.1

Ratio 10



Type 6

Fiber length distribution in the web, after processing the mat through the nip-rollers (1) and the vacuum-roller (2)



Appendix C

Yarn Modulus as a Function of Helix Angle

Appendix C

Yarn Modulus as a Function of Helix Angle

$$\sigma_y = \sigma_f \cos^2 \Theta$$

$$\varepsilon_f = \varepsilon_y \cos^2 \Theta$$

when yarn breaks $\varepsilon_y = \varepsilon_f$ at center of yarn

$$\therefore \quad \frac{\sigma_{y\,Break}}{\varepsilon_{y\,Break}} = E_y = E_f \cos^2 \Theta$$

where Θ = helix angle

σ_y = yarn stress

ε_y = yarn strain

σ_f = fiber stress

ε_f = fiber strain

E_y = yarn modulus

E_f = fiber modulus

APPENDIX D

COMMERCIAL BINDERS

BORDEN CHEMICAL
DIVISION OF BORDEN INC
THERMOPLASTICS DIVISION / POLYCO DEPARTMENT
511 LANCASTER STREET / LEOMINSTER, MASS. 01453
Telephone: (617) 537-1711 Teletype 710 347-0252

BORDEN

DATA SHEET

POLYCO 571

Polyvinyl Acetate Homopolymer Emulsion, Large Particle Size, Ethanol Stable

Fields of Use

Many applications in general adhesive formulations, consumer packaging adhesives, textile finishes, and industrial coatings.

Properties

Solids Content	55 ± 1.0
Viscosity at 25°C. (Brookfield LVF)	1700 - 2500 cps
pH @ 25°C.	4.0-5.0
Particle Size (approx.)	2-7 microns
Free Monomer	0.5% max.
Specific Gravity of Emulsion @ 25°C.	1.10
Weight per U.S. Gallon @ 25°C.	9.2 lbs.
Freeze/Thaw	Pass
Emulsion Type	Nonionic
Film Description	Hazy
Blocking Temperature (5 psi, overnight, 3 mil coating)	134° - 138°F.
Heat Seal Temperatures (50 psi, 4 sec. 1.2 mil coating)	250° - 375°F.

POLYCO 571 is a general purpose, unplasticized, polyvinyl acetate emulsion which displays excellent stability to water soluble solvents. Such stability permits a wide range in the choice of additives for formulating.

For lower viscosity ranges, see data sheets on POLYCO 117-SS and POLYCO 561.

Data Sheet 0574

BORDEN CHEMICAL
DIVISION OF BORDEN INC
THERMOPLASTICS DIVISION
511 LANCASTER STREET / LEOMINSTER, MASS. 01453
Telephone: (617) 537-1711 Teletype 710 347-0252

BORDEN

DATA SHEET

POLYCO 2140
Polyvinyl Acetate Latex

Fields of Use

Pigment binder for paper and paperboard coating, fiberglass sizing, and non woven binder. Has found utility in hardboard coating.

Properties

Solids Content	47 ± 0.5%
Viscosity (Brookfield LVF, 25°C., 60 rpm)	100 cps. (max.)
pH	6.3 - 7.3
Particle Size	0.20 micron (avg.)
Surface Tension	38 - 42 dynes/sq. cm.
Density, 25°C.	9.0 lbs./gal.
Mechanical Stability	Very Good
Chemical Compatibility	Very Good
Odor	Very Low
Non-Yellowing Properties	Very Good

POLYCO 2140 is a fine particle size polyvinyl acetate latex specifically designed and developed to meet the requirements of the paper and paperboard coating industry.

POLYCO 2140 has low foaming properties, low odor, excellent stability to mechanical shear and is compatible with a wide range of other coating binders, pigments and additives, giving low viscosities in a wide range of formulations. POLYCO 2140 may be added to styrene/butadiene coatings to improve block resistance, stiffness, ink receptivity, glueability, and porosity.

Coatings prepared with POLYCO 2140 have exceptionally high pick resistance due to the presence of functional groups which impart specific adhesion to cellulose. POLYCO 2140 coatings also exhibit good glueability, low odor, improved brightness, resistance to yellowing on aging, and excellent resistance to blistering with heat set inks.

POLYCO 2140 may also prove of interest in such applications as textile coatings, non-woven fabric stauration, fiberglass sizing, and other related fields. As a hard non-woven binder, POLYCO 2140 has good resiliency and moderate resistance to washing.Improved dry cleanability can be obtained by adding a melamine formaldehyde resin.

BORDEN CHEMICAL
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THERMOPLASTICS DIVISION
511 LANCASTER STREET / LEOMINSTER, MASS. 01453
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DATA SHEET

POLYCO 2151

Vinyl Acetate/Acrylic Copolymer Emulsion

Fields of Use

Interior, Semi-Gloss and Exterior Emulsion Paints.

Properties

Solids Content	54.0 - 56.0%
Viscosity @ 25°C. (Brookfield LVF, 3/30)	400 - 1000 cps.
pH @ 25°C.	4.5 - 5.5
Particle Size	0.1 - 0.8 microns
Free Monomer	0.5% max.
Specific Gravity of Emulsion @ 25°C.	1.09 g/cc.
Weight per U.S. Gallon @ 25 C.	9.10 lbs.
Film Hardness	Soft and Flexible
Film Clarity	Good to Very Good
Film Gloss	Good to Very Good

POLYCO 2151 is a uniquely designed vinyl/acrylic copolymer emulsion, the product of several years of concentrated research, which combines in a single product the key interior paint properties of good levelling (or flow) and excellent scrub resistance. 100% acrylic emulsions have given this desirable combination of properties, at a high premium in cost, but there has been no vinyl acetate based emulsion offered to date which could claim both levelling and scrub resistance. The claims made above are based on exhaustive evaluations of many commercial polymers in a wide variety of interior flat paint formulations. POLYCO 2151 offers the paint formulator the flexibility of formulating at high PVC without excessive deterioration in scrub resistance while, at the same time, achieving better apparent hiding due to the better levelling or flow of the paint.

In interior paints, POLYCO 2151 also exhibits very good low temperature coalescence, enamel holdout and color acceptance (aqueous and "universal aqueous" systems as well as "universal" oleoresinous systems - the latter sometimes requiring minor formulation modifications).

POLYCO 2151 has been evaluated and is being used commercially as a semi-gloss paint base. The superior levelling observed in interior flats is also apparent in such semi-gloss paints.

Exposure data on POLYCO 2151 indicates that the product gives commendable exterior durability which makes possible a single, high performance vinyl/acrylic for all three major trade sales areas of application - interior flat, semi-gloss and exterior. (Note: Maximum exterior durability, especially over unpainted wood, can only be achieved by using a product specifically designed for exterior wood. Inquiries on POLYCO 2358, designed for exterior, will be welcome).

Data Sheet
291-375-5C

BORDEN CHEMICAL
DIVISION OF BORDEN INC
THERMOPLASTICS DIVISION
511 LANCASTER STREET / LEOMINSTER, MASS. 01453
Telephone: (617) 537-1711 Teletype 710 347-0252

BORDEN

DATA SHEET

POLYCO 2445
Styrene/Butadiene Copolymer Latex

Fields of Use

Pigment Binder for Paper & Paperboard Coating

Properties

Solids Content	50 ± 1.0%
Viscosity @ 25° C. (Brookfield LVF 1/60)	100 cps. (max.)
pH	5.0-6.0
Free Monomer	0.1% (max.)
Particle Size	0.30 microns (av.)
Surface Tension	38 - 42 dynes/cm.
Density, 25° C.	8.5 pounds/gallon

POLYCO 2445 is a unique carboxylated styrene/butadiene latex specifically designed to meet the requirements of the paper and paperboard coating industry.

The excellent shear stability, chemical compatibility, low foaming characteristics and desirable rheological properties exhibited by POLYCO 2445 in a wide range of clay coating recipes insures trouble-free formulation and ease of application of POLYCO 2445 bound coatings.

The superior pick strength, water resistance, gloss, non-yellowing and ink holdout characteristics of POLYCO 2445 affords superior print fidelity. Preliminary data indicates that POLYCO 2445 will give outstanding gloss development and minimum sticking on high temperature gloss calendering.

Of particular interest is the excellent stability of POLYCO 2445 over a wide coating pH range, and its outstanding water resistance when used in starch coatings. Because of its good chemical stability, POLYCO 2445 may be used in combination with other emulsions such as POLYCO 2140, a hard polyvinyl acetate latex, or POLYCO 2719 a soft acrylic latex.

In blending POLYCO 2445 and POLYCO 2140, excellent pick strength is afforded by POLYCO 2445, while POLYCO 2140 imparts stiffness, block resistance, brightness, porosity, low odor and yellowing resistance to the coating.

Data Sheet 220-475-5C

BORDEN CHEMICAL
DIVISION OF BORDEN INC
THERMOPLASTICS DIVISION
511 LANCASTER STREET / LEOMINSTER, MASS. 01453
Telephone: (617) 537-1711 Teletype 710 347-0252

BORDEN

DATA SHEET

POLYCO 2607

Internally Plasticized Vinyl Chloride Latex

Fields of Use

Paper and fabrics coatings, binder for water based inks, binder for non-wovens.

Properties

Solids Content	55 ± 1.0%
pH	7.0 - 8.5
Surface Tension	41 - 44 dynes/cm.
Specific Gravity	1.070 - 1.090
Viscosity @ 25°C. (Brookfield LVF 2/60) cps.	200 max.

POLYCO 2607 is an internally plasticized latex and yields clear, highly flexible films with good water resistance.

POLYCO 2607 produces coatings with excellent gloss even when highly loaded. It can be readily compounded to give flame retardance.

The block resistance and hardness of POLYCO 2607 may be improved by adding 10% - 30% of POLYCO 2612.

Data Sheet 179-175-1C

BORDEN CHEMICAL
DIVISION OF BORDEN INC
THERMOPLASTICS DIVISION / POLYCO DEPARTMENT
511 LANCASTER STREET / LEOMINSTER, MASS. 01453
Telephone: (617) 537-1711 Teletype 710 347-0252

BORDEN

DATA SHEET

POLYCO 2618
Pre-Plasticized Vinyl Chloride Copolymer

Fields of Use

Spray bonding or saturation of non-wovens, particularly where higher dielectric bonds are required.

Properties

Solids Content	56 ± 1.0%
pH	9.0 - 10.0
Viscosity @ 25°C. (Brookfield FVF 1/30)	100 cps. max.
Surface Tension	32-38 dynes/cm.
Weight per Gallon	9.4 lbs.

POLYCO 2618 is a pre-plasticized version of POLYCO 2612 and is designed as a binder for non-woven webs where improved heat sealing bonds are required.

POLYCO 2618 is plasticized with an ester type plasticizer. Its films exhibit high gloss, good heat and light stability, and excellent dielectric sealability. It offers improved mechanical and chemical stability over previous products of this type.

Data Sheet 062-0971

National / RESINS

TEXTILE DIVISION

NATIONAL STARCH AND CHEMICAL CORPORATION • EXECUTIVE OFFICES: 750 THIRD AVENUE, NEW YORK, N.Y. 10017

RESYN® 1014

DESCRIPTION: Resyn 1014 is a polyvinyl acetate homopolymer.

TYPICAL LATEX PROPERTIES:

SOLIDS	*55%*
pH	*4.5*
PARTICLE SIZE	*0.3 Microns*
PARTICLE CHARGE	*Anionic*
[1] VISCOSITY	*800 CPS*
DENSITY @ 72°F.	*9.2 lbs./gal.*
BORAX STABILITY	*Excellent*

TYPICAL FILM PROPERTIES:

[2] HARDNESS	*26 SRH*
FLEXIBILITY	*Mod-flexible*
CLARITY	*Clear*
[3] TENSILE	*1800 PSI*
[3] ELONGATION	*0%*
WATER RESISTANCE	*Good*
REFRACTIVE INDEX 30°C.	*1.4652*

STORAGE AND HANDLING: Under normal storage conditions Resyn 1014 displays excellent stability. No special handling precautions are required.

USAGE: Resyn 1014 is quite useful in carpet backcoatings, pile fabric backcoatings, dimensional stabilization and hand building, as well as in several semi-durable finishes including felts, laces, curtains, buckrams, crinolines, tickings, nettings, interlining, nylon hosiery and many others.

FURTHER INFORMATION: A National sales representative would be pleased to discuss this or any other National product with you. Please also feel free to contact our research laboratories directly:

National Starch and Chemical Corp.
Textile Division
1700 West Front Street
Plainfield, New Jersey 07063

Telephone 201/755–4100

[1] LVF Brookfield, #3 Spindle, 60 RPM @ 72° F.

[2] Sword Rocker Hardness – Measured @ 72° F. on 1.5 mil (wet) force dried film cast on plate glass.

[3] Instron Tensile Tester using 10 mil (approx.) air dried films. Speed of jaw separation was 0.2"/minute.

29968

National RESINS

TEXTILE DIVISION

NATIONAL STARCH AND CHEMICAL CORPORATION • EXECUTIVE OFFICES: 750 THIRD AVENUE, NEW YORK, N.Y. 10017

RESYN® 1048

DESCRIPTION: Resyn 1048 is a polyvinyl acetate latex.

TYPICAL LATEX PROPERTIES:

SOLIDS	55%
pH	4.6
PARTICLE SIZE	1 Micron
PARTICLE CHARGE	Non-ionic
[1]VISCOSITY	1200 CPS
DENSITY @ 72°F	9.2 lbs./gal.
[2]MECHANICAL STABILITY	Good

TYPICAL FILM PROPERTIES:

[3]HARDNESS	38 SRH
CLARITY	Slightly Cloudy
FLEXIBILITY	Brittle

STORAGE AND HANDLING: Under normal storage conditions Resyn 1048 displays excellent stability. No special handling precautions are required. Efficiency as a fiberglass forming size may be impaired by freezing.

USAGE: Resyn 1048 exhibits high strand integrity and good "choppability" when used as a forming size for fiberglass.

FURTHER INFORMATION: A National sales representative would be pleased to discuss this or any other National product with you. Please also feel free to contact our research laboratories directly:

National Starch and Chemical Corp.
Textile Division
1700 West Front Street
Plainfield, New Jersey 07063

Telephone 201/755-4100

[1] LVF Brookfield, #3 Spindle, 60 RPM a 72°F.
[2] Hamilton Beach Mixer - 15 minutes a 10,000 RPM.
[3] Sward Rocker Hardness-Measured a 72°F. on 1.5 mil (wet) force dried films cast on plate glass.

29968

RESIN DIVISION

BULLETIN No.

National STARCH and CHEMICAL CORPORATION

NEW YORK

Technical Service Bulletin

RESYN® 2211

TYPICAL PROPERTIES

DESCRIPTION	Vinyl Acetate Copolymer Emulsion
SOLIDS	55%
pH	4.9
PARTICLE SIZE	1.0 Microns (Average)
[1]VISCOSITY	1000 cps.
LBS./GAL	9.2 @ 72°F
RESIDUAL MONOMER	0.5% Maximum
[2]INTRINSIC VISCOSITY	2.0

[1]Brookfield Viscosity - Model LVF #3 Spindle 60 RPM @ 72°F.

[2]Intrinsic Viscosity of the Polymer as measured in Acetone @ 30°C.

(over)

18171
supersedes
17266

National RESINS

TEXTILE DIVISION

ATIONAL STARCH AND CHEMICAL CORPORATION • EXECUTIVE OFFICES: 750 THIRD AVENUE, NEW YORK, N.Y. 10017

RESYN® 2833

DESCRIPTION: RESYN 2833 is a soft self-reactive vinyl acrylic terpolymer latex.

TYPICAL LATEX PROPERTIES:

SOLIDS	*45%*
pH	*4.6*
PARTICLE SIZE	*0.14 Micron*
PARTICLE CHARGE	*Anionic*
[1] VISCOSITY	*300 cps.*
DENSITY @ 72°F.	*8.8 lbs./gal.*
[2] MECHANICAL STABILITY	*Good*

TYPICAL FILM PROPERTIES:

[3] HARDNESS	*0 SRH*
FLEXIBILITY	*Flexible*
CLARITY	*Clear*
[4] TENSILE STRENGTH	*235 psi.*
[4] ELONGATION	*725%*
WATER RESISTANCE	*Good*
SOLVENT RESISTANCE	*Good*
REFRACTIVE INDEX 24°C.	*1.469*
GLASS TRANSITION TEMP.	*-29°C.*

STORAGE AND HANDLING: Under normal storage conditions RESYN 2833 displays excellent stability. No special handling precautions are required.

USAGE: The properties of RESYN 2833 make it suitable for flocking, pigment binding, textile backcoating, nonwoven fabric binding, automobile and upholstery backcoating, cotton flote as well as various durable and semi-durable textile finishes.

FURTHER INFORMATION: A National sales representative would be pleased to discuss this or any other National product with you. Please also feel free to contact our Research Laboratories directly:

National Starch and Chemical Corp.
Textile Division
1700 West Front Street
Plainfield, New Jersey 07063

Telephone 201/755-4100

[1] LVF Brookfield #3 Spindle, 60 RPM @ 77°F.

[2] Hamilton Beach Mixer – 15 Minutes @ 10,000 RPM.

[3] Sward Rocker Hardness – Measured @ 72°F. on 1.5 mil (wet) force dried films cast on plate glass.

[4] Instron Tensile Tester using 3 mil (approx.) films dried @ 72°F. Crosshead speed was 2.0"/minute.

30769
supersedes
29968